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NUCLEONICS

October, 1947

NUCLEAR CHEMISTRY PROBLEMS

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SEPARATION OF STABLE ISOTOPES

RADIOACTIVITY UNITS AND STANDARDS

ISOTOPE TECHNIQUES IN BIOCHEMISTRY—II

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RADIATION CHEMISTRY AND PHOTOCHEMISTRY SYMPOSIUM

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ADVISERS

John R. Dunning
H. H. Goldsmith

CONSULTANTS

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Clark Goodman
F. C. Henriques, Jr.
S. D. Kirkpatrick
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NUCLEONICS

THE McGRAW-HILL MAGAZINE OF NUCLEAR TECHNOLOGY

Reporting Advances in Nuclear Technology

THE ESSENTIAL FACTS and concepts underlying the wartime development of nuclear fission reactors (atomic bombs and piles) were known to nuclear physicists throughout the world by the year 1940. It was therefore only the threat of German atomic bombs that caused fundamental scientists to make an all-out attack on the engineering aspects of nuclear fission.

The hundreds of declassified technical documents now trickling from the archives of the United States nuclear energy project represent facts of nature which it would be illogical to assume were still unknown to centers of nuclear research in other parts of the world. They are being declassified to prevent further United States nuclear development from being stifled, just as chemical research might be stifled if the discovery of a powerful new chemical explosive removed large areas of chemical investigation from publication.

If nucleonics were evaluated in terms of its potential growth, it would have to be regarded, of course, as still in its infancy. But if measured by the capital and man-hours presently being expended collecting data, integrating results, and building nuclear engines, machines, and devices, we would see that the field has far outgrown the capacities and boundaries of previously existing technical publications. Therefore, if the reporting of advances in nuclear science and engineering is to fulfill its traditional purpose of stimulating broader participation in the development of new ideas, new approaches to the dissemination of information in this field will have to be evolved.

A step toward the solution of some of the problems posed by expanding activity in the nuclear energy field has been made by the founding of NUCLEONICS. This journal will make available a disinterested medium for reporting important advances in all phases of applied nuclear physics.

The task of synthesizing and interpreting the great technological progress of recent years now rests on the shoulders of a comparatively small inner circle of fundamental and applied nuclear scientists. The reviews and reports they have recently resumed contributing to the technical literature are even now feeding back to them in the form of fresh attacks on unsolved problems, made by new colleagues drawn from other parts of the scientific and engineering worlds.

Thus the slowly growing freedom of scientific reporting is already proving a powerful stimulus to the productive interplay of ideas. It is resulting in more rapid, economical, and fruitful development of our nuclear science and technology. —*W.M.D.*

Some Problems for Study in Nuclear Chemistry*

A review of the techniques and accomplishments of nuclear chemistry by a major contributor to its development. The significance of this field for the nuclear power industry and other areas of chemistry, physics and industry is pointed out—together with new opportunities for chemists

By CHARLES D. CORYELL

Department of Chemistry, Massachusetts Institute of Technology

NUCLEAR CHEMISTRY is a field of activity as old as nuclear physics. The workers in the late nineties made studies of the possible influence of chemical binding on radioactive properties, with the result that a number of new elements were discovered, existing only in radioactive forms. Nuclear science remained predominately in the hands of physicists, however, even on the chemical side and in spite of the vast chemical implications of developments in nuclear transmutation and artificial radioactivity that have made available radioactive forms of all of the chemical elements.

The developments in atomic energy of the last few years give promise that the chemists of the world will now play a more prominent role in nuclear research, and that nuclear chemistry will achieve greater importance as a part of chemical science rather than as an operational appendage of nuclear physics. Outlined here are some new activities and some challenging problems in several subdivisions of nuclear chemistry.

Industrial Nuclear Chemistry

Radioactivity has been the basis for industrial operations in the limited field of radium production [Ra^{226} and $MsTh_1(Ra^{228})$] and the processing of a few other materials from the natural radioactive series. In the late thirties there was the promise of the development of various artificially radioactive preparations from cyclotron production. The industrial development of nuclear fuels, in particular by pile operation involving the large scale synthesis of unstable nuclear species in massive amounts, has led to almost explosive expansion of a new nuclear power industry. This development, under eager support of national governments because of the great military implications, already offers employment to hundreds of chemists and chemical engineers.

Little detail can be given about the chemical problems of the nuclear power industry, but the general outline of the problems was clear from the Smyth report (*1*), and certainly a great deal of progress must have been made from the intensive studies in wartime that led to the over-all technical success of nuclear explosives. There certainly are many interesting chemical problems in the geochemistry of uranium and thorium, and in the processing of the ores, the purification of compounds of these elements, and their preparation for industrial processing.

A larger variety of chemical problems and the most characteristic new problems of industrial nuclear chemistry are undoubtedly associated with pile operation rather than with separation of uranium isotopes, so emphasis will be given to this type of nuclear power procedure in this paper. The operation of nuclear fission piles at high power levels brings forth a host of chemical questions, many related to the properties of materials of special neutron-physical characteristics, and many related to the behavior of mate-

*Taken from material presented at the Conference of Nuclear Chemistry sponsored by the Chemical Institute of Canada, McMaster University, Hamilton, Ont., May 15–17, 1947.

rials under intense radiation, especially in fields of high neutron flux. Other people (*2*, *3*) have discussed the primary processes of radiation chemistry and given a brief introduction to the field. There is quite a challenge here in work on the production of industrial power from nuclear sources.

Large groups of chemists and engineers have been preoccupied with the chemical bases for separation of fissile materials from fuel material exposed in a pile, which has also become contaminated by the extraordinarily radioactive fission products, but the optimum procedures can hardly have yet been developed. Chemical bases for the recovery of partially used fuel material and the convenient disposal of radioactive wastes undoubtedly deserve more attention in a nuclear power industry operating under long-term or peacetime schedule. Special techniques are required for the economical purification and special fabrication of recovered fissile materials for subsequent use.

The problems of chemical operations on intensely radioactive materials are not unique with the nuclear power industry, but they dominate the field and limit in many cases the scope of operations. There is certainly a great need for new ideas and new techniques in remote control operations, at the unit operation level and in multistage work, as well as in research operations on the laboratory scale. Indeed one of the great advantages that the nuclear industry offers to chemical research and development is the production and dissemination of large quantities of radioisotopes from the fission-product group of elements and by neutron activation of materials exposed in the pile. The availability of many of these in useful form and in high purity will depend on the development of new techniques for isolating them economically and conveniently. Many ideas on operations will undoubtedly come from laboratories which are recipients of the radioactive materials at high activity levels and in which techniques must be developed for convenient utilization of these materials.

There are certain implications to science as a whole that derive from the present nationalistic stamp of the nuclear power industry. Provisions of secrecy—miscalled security—cloak much of the work, and prevent the publication of fundamental information, the disclosure of useful techniques, and the stimulation of cross-fertilization of ideas, open competition, and independent check. In the present phase there is a shortage of manpower, and consequent danger of domination of the work by operational deadlines, to the detriment of thorough investigation of fundamental reactions and adequate correlation of the various activities of groups that may be separately compartmented.

Traditional Problems of Nuclear Science

There is a group of problems involving nuclear chemistry that follow naturally from the pattern of development in the decade before the last war. Given added importance and scope by the wartime developments, many of the problems are well suited to academic research although many of them require access to and often propinquity to a source for nuclear transformation—high-voltage accelerator, cyclotron, or pile.

Although about 500 different artificially radioactive nuclides* have been identified (*4*, *5*), the search for new ones is still in progress, and there is a tremendous amount of work to be done in the adequate characterization of most of those already reported. In fact, the decay schemes are known reliably for only a very few γ-emitting nuclei. Much of the research will be aided by improvements in chemical separation and in purification.

Some specific examples may be cited from the fission-product field (*5*, *6*). It would appear that almost all of the medium-lived fission products of reasonable fission yield (nearly 200)

* Dr. T. P. Kohman of the University of Chicago has suggested the word *nuclide* for an atomic species with a given nuclear configuration, recommending the reservation of the word *nucleus* for the nucleus proper.

have been reported but details of the decay process are less well known—in particular, the quantitative relations among β energies and γ energies in complex decays, and relations involving conversion electrons. Furthermore, the field is so large and important that it merits continued work, and since the range of elements produced extends from $_{30}$Zn through $_{63}$Eu, chemical problems are dominant.

Some careful chemical work needs to be done in the search for and characterization of species that appear to be exceedingly long-lived: Se^{79}, Zr^{93}, Pd^{107}, I^{129}, Cs^{135}, and Sm^{151}. A great deal of useful chemical work can be done on species of half-life less than 2 hours. Indeed, there is a rich reward in new information in fission-product chemistry and in nuclear physics for those who will develop rapid methods of separation of fission elements from one another in times of the order of minutes or less. In particular, the detailed identification of fission products emitting delayed neutrons is an important problem. The 55.6s and 22.0s activities have been identified by Snell and co-workers as Br^{87} and I^{137} (*5*, *7*) and the 4.51s activity has recently been identified by Sugarman as $Br^{>86}$ (*8*).

There is also a rich field for analytical research in quantitative methods of separating the fission-product elements and determining them. Almost any contribution to the general chemistry of these elements will be a contribution to the nuclear chemistry, and many studies of their general chemistry can be aided by the use of radioactive tracers.

The identification and characterization of nuclides of the heaviest elements is more restricted as a field for university research, since so much seems to have been done in connection with military programs, part of which may remain secret for a long time, and certain starting materials such as Pu^{239} are likely to be restricted for some time. Groups at Chicago (*9*) and at Chalk River (*10*) have elucidated the properties and the chain relationship attainable among the nuclides of the $4n + 1$ radioactive decay series, starting with Am^{241}, including Np^{237} and U^{233}, and extending to Bi^{209}. Seaborg recently reviewed (*11*) some work of his group on trans-Th species.

For the large majority of elements, the radioactive species of medium life from common nuclear reactions are moderately well known, although there is a deficiency of knowledge about nuclei with an excess of protons over the stable configurations. Proton bombardments have been studied less extensively than deuteron bombardments, and the results of bombardments of high-energy particles have been studied only recently. It is probable that many more examples of excited isomers of stable and radioactive nuclei will be encountered, and some of these may give the chemist more opportunity of studying the chemical changes consequent on isomeric transition.

With the construction of new nuclear machines leading to γ-ray energies and projectile energies in the region of several hundred Mev, complicated nuclear reactions are being reported that involve multiple evaporation of nucleons from the compound nucleus produced in the bombardment (*12*). The interpretations of the transmutations achieved may bring added interesting problems to the nuclear chemist because of low yields and multiplicity of competitive nuclear reactions.

A more conventional chemical occupation is the study of the chemical properties of elements whose isotopes have only transitory existence or which are the products of nuclear synthesis and thus available generally only in small or tracer quantities. Thirteen of such elements are tabulated here, including atomic numbers 43, 61, and 84–96 inclusive except for $_{90}$Th and $_{92}$U. Reference is made in the table only to the longest-lived isotope, identified by mass number, half-life, decay process, and mode of origin. Decay products of natural radioactive elements are identified as "Nat.," fission products or products of uranium pile operation are noted, and, in the case of products

Elements of Transitory Existence

Atomic number	*Symbol*	*Best isotope*	*Half-life*	*Decay*	*Origin*
43	Tc[a]	99	4×10^6 y	β	Fission, Bomb. Mo
61	Pm[b]	147	3.7 y	β	Fission, Bomb. Nd
84	Po	210[g]	140 d	α	Nat.
85	At[c]	211	7.5 h	α	Bomb. Bi
86	Rn	222	3.8 d	α	Nat.
87	Fa[d]	223	21 m	β	Nat.
88	Ra	226	1590 y	α	Nat.
89	Ac	227	13 y	1 %α, β	Nat.
91	Pa	231	3.2×10^4 y	α	Nat.
93	Np	237	2.25×10^6 y	α	Pile, Bomb. U
94	Pu	239	2.4×10^4 y	α	Pile, Bomb. U
95	Am[e]	241	500 y	α	Bomb. Pu
96	Cm[f]	242	150 d	α	Bomb. Pu

[a] Technetium
[b] Promethium (unofficial)
[c] Astatine
[d] Francium
[e] Americium
[f] Curium
[g] Po^{208} has a longer half-life but is far less accessible for general study.

of bombardment, a suitable target element is included after the word "Bomb." The discovery and naming of these elements have been discussed by Paneth (*13*).

In the first work on any of these elements, the chemical properties had to be inferred from the chemical partition of tracer amounts, followed radioactively, in the reactions of similar elements. If the half-life is sufficiently long, milligram or gram quantities of natural radioactive materials or principal pile products may be accumulated, and microgram or milligram amounts of bombardment products may be produced. Under these circumstances, microchemical studies can be made to give almost all chemical information that could be obtained from macro amounts of material.

Ra, for instance, has been obtained in large quantities, but work on the semi-micro scale is generally preferred because of the penetrating radiations arising from its decay products. Pa is available in decigram amounts. Workers on government projects may have access to Pu in gram amounts or greater, and Np can be produced as a byproduct of pile operation in visible quantities. Precautions must be taken against the toxicity of even microgram amounts of these elements. It is also to be expected that milligram amounts of Tc and element 61* will be isolated from fission-product mixtures. One milligram of 61^{147} will represent, however, 0.6 curie of radioactivity, an amount that might lead to extensive radiation-induced decomposition of compounds under macroscopic study. It seems as if At and Fa are accessible to study only on the tracer scale because of the very short half-lives of all their isotopes.

A number of properties of elements can be determined from tracer studies. Virtually all of our information on Po, for instance, comes from such studies. It is apparent on examination of the problems that much more knowledge can be obtained with a sharpening of quantitative techniques. The only element listed in the table for which a tracer supply is, in principle, hard to maintain is 7.5h At^{211} which has to be made with a cyclotron of high α energy

* The long-lived isotope was discovered (*5*) in studies of fission products independently by N. E. Ballou of the United States Atomic Energy Project and by B. Goldschmidt and F. Morgan of the Canadian Project. J. A. Marinsky and L. E. Glendenin of the Clinton Laboratories in Oak Ridge used ion exchange absorption column separations to give absolute chemical identification of the element, the first achieved for activities of element 61. They propose the name *Promethium* for this element.

and which would be difficult to transport far. It is to be hoped that macro amounts of Np and Pu and tracer solutions of Am and Cm will soon be widely available for fundamental chemical studies.

Applied Radiochemistry

The production of radioactive species of all elements of the periodic system should have given a great impetus to all inorganic chemical research. The impetus was slow in being felt partly due to the specialization of nuclear physics, partly due to the lack of familiarity to chemists of the techniques of radioactive measurement, and partly due to the complications of the production and measuring equipment. The conclusion seems inescapable, however, that chemists closed their eyes to many opportunities, especially chemists in university communities where cyclotrons were available. The situation is changing rapidly now because the current great impetus as a result of the nuclear power projects is arousing widespread interest in chemical circles.

It can now fairly be said that the needs of nuclear chemistry will revivify many dormant fields in inorganic chemistry. Nuclear chemistry demands increased knowledge of many inorganic reactions of both common and rare elements. More important, it offers useful machinery for the studying of new reactions, of reaction mechanisms, and of equilibria involving the separation of solids and gases, including those of complex formation. There is a fruitful field of study in that of the exchange of atoms, radicals, or complex addenda among various complexes or forms of different valence state. It appears that there is a correlation between valence state exchange and ready reversibility of electrode reactions; the reported lack of exchange between $Fe(CN)_6^{=}$ and $Fe(CN)_6^{--}$ appeared to contradict this until it was established recently by W. B. Lewis at M.I.T. that this exchange is rapid.

Some more of these possibilities have been discussed elsewhere (*2*), including the tremendous possible applications of C^{14} to organic chemistry, biochemistry and medicine.

Analytical procedures can be greatly simplified and results obtained more quickly if the constituent being determined is a radioactive one. If the constituent is inherently radioactive, extraordinary sensitivity can be obtained; for instance, 10^{-10} gm of Pu^{239} will give in a thin sample a counting rate of about 10 α counts per minute, easily detectable. Radiochemical analysis for tracer activity of an element is commonly made by addition of a known mass of inert form of the element for carrier followed by rapid but effective purification of the element, the yield being established by the recovery of carrier. Conversely, a difficult isolation of an inactive constituent before analysis can be simplified by the addition of a known amount of tracer to serve as a measure of chemical yield and simplified chemistry can be employed followed by determination of quantity and radioactivity. It is very easy to use radioactive tracers to determine the sharpness of chemical separations, or to measure mechanical losses. It should be pointed out that the precision of radioactive counting can rarely be made greater than about 1% probable error, but the range of concentration that can be measured is large, and quite low concentrations can be studied with tracers of high specific activity.

There is promise that chemical analysis can be made very readily for those elements with high neutron activation cross section by timed exposure of a known mass to a known high neutron flux, as from a pile, followed by determination of the amount of induced radioactivity, identified after minimal chemistry, if any, by half-life and radiation absorption characteristics.

Tracers offer certain advantages in the study of surface chemistry, the interactions of catalysts with substrate, and the mechanisms of catalyzed reactions. They have also been used to determine the rates of chemical reaction at equilibrium. Fairly extensive studies have already been carried out

on the mechanisms of biological reactions and the metabolism of rare elements. In biological systems the self-registering action of radioactive materials on photographic plates, radioautography, is a useful technique. Eventually radioactive materials may be expected to find wide industrial use in the study of coatings, corrosion, and leaks, in process control, in assay *in situ*, and in secret marking. Since other authors (*2*) have covered applications of radioactive and stable tracers in a variety of systems, further elaboration will not be made here.

Fundamental Physical Problems Involving Chemistry

In nuclear science the borderline between chemistry and physics is often undetectable, and much of the work requires experience in both fields and also a collaborative attack. Both chemists and physicists will rejoice when a more general answer is available to the problem of absolute counting, especially of β rays, γ rays, and X-rays. This problem is largely dependent on the satisfactory quantitative unraveling of the decay mechanisms of a larger number and variety of nuclei to serve as calibrating substances, and on an appreciation of the empirical problems of scattering, absorption, and the elusive factor called "geometry." These problems are both diffuse and obtuse, and the chemist must be aware of them in his own work and may be able to aid the physicist in the critical evaluation of experiments.

We may also hope for an increase in our understanding of β-decay processes and of isomeric transition and internal conversion. The general increase in knowledge should help to clarify the principles of nuclear structure for unstable and stable nuclei, for which we have only a general picture (*14*).

Extensive chemical operations are required in programs to determine the nuclear properties of unstable nuclei, such as neutron cross section, nuclear spin, magnetic moment, and nuclear level density. The same is true in programs to determine the variation of cross sections for nuclear reactions as a function of the energy of the projectile (nuclear excitation functions) and the relations among the yields of competitive nuclear reactions.

There is much to be done in the detailed quantitative study of the yields of fission products. One would expect fine structure in the curve for the thermal fission yield of U^{235} products as a function of mass number, because of delayed neutron emission, coincidental α emission, or irregularities in the stability of primary fission products. The use of the mass spectrometer for precision fission-yield determinations of Kr and Xe has been discussed elsewhere (*2*, *15*), but standard chemical methods are required for most fission products and adequate precision has not yet been obtained. No study of the yield-mass curve has been reported for fission produced by high energy neutrons, or for change in the fissile nucleus or with the manner of producing fission (*e.g.*, γ-induced fission or spontaneous fission).

Another attractive but difficult problem is that of establishing the distribution of primary charge in the fission products, which may be attacked through a quantitative study of the fission yields of shielded nuclei [Glendenin, Coryell, Edwards, and Feldman (*5*)], of the very short-lived fission products as separated by gas-sweeping [Turkevich, Dillard, Adams, and Finston (*5*)], or of the delayed neutron emitters.

Fundamental Chemical Problems

In the development of chemical procedures for the quantitative analysis of the activities of fission products it has been noticed that quantitative recovery is difficult for certain radioactive elements. Evidence exists that I, formed as a result of nuclear transformation, occurs in appreciable fractions in forms which are imperfectly brought into reaction by carrier I in the ordinary valence states from -1 to $+7$. Besides being an obstacle to chemical operations on radioactive I, this represents a challenge to the nu-

clear chemist, who should be able to understand the chemical behavior of the species he deals with.

Some studies have also been carried out by exchange experiments on the valence state of I formed as a result of the decay of Te in known valence state. These results indicate that I in valence level -1, 0 or $+1$ is formed to considerable extent from the decay of both $TeO_3^=$ and $TeO_4^=$. Similar studies should be carried out with other elements showing more than one stable oxidation level. Similar evidence exists also that radioactive Zr also occurs in part in forms that react but slowly with carrier Zr unless very stable complex-formers are present which induce exchanges. Hydrolysis and colloid-formation of Zr solutions may furnish the explanation in this case.

The attack on problems of this type is dependent in part on the knowledge of the chemical reactions of substances at trace concentrations—below 10^{-7} molar. Radioactive substances prepared without carrier furnish the best materials for the study of reactions at such low concentrations. Fields for study include those of reaction rates, equilibria, electrochemical properties, and radiocolloid formation.

Another more difficult field for investigation is the chemical state of atoms formed in the solid state by nuclear reactions. The S^{35} formed in KCl by the reaction of $Cl^{35}(n,p)S^{35}$ appears in the work of R. R. Edwards of M.I.T., for instance, to be in a state that exchanges rapidly and completely with $SO_4^=$ under a variety of conditions of dissolution.

Analogous reactions occurring in solution and gas phases are ascribed to the "hot" atoms with considerable recoil energy immediately following nucleogenesis. Edwards has found that a large fraction of the S^{35} formed by the same reaction in CCl_4-CS_2 mixtures is found in CS_2 although elementary S and CS_2 show no exchange of S atoms.

A well-known field of nuclear chemistry based on the special properties of recoil atoms is that of the Szilard-Chalmers reaction, wherein the radioactive atoms from neutron activation separate themselves from the bulk of material being irradiated. A similar separation process is found to occur in cases of isomeric transition when conversion of the γ ray occurs. Much more needs to be known about the mechanism of such separations, its dependence on the type of compound used, and the conditions governing back-reaction. It is felt that the efficiency of the Szilard-Chalmers reaction is impaired by operations at very high irradiation intensities, probably because of general radiation decomposition.

An important procedure in nuclear chemistry is that of coseparation of a tracer material with a compound of other elements. Certain hydrous precipitates such as LaF_3, MnO_2, or $Fe(OH)_3$ have been widely used to carry tracer substances of a variety of sorts, and to separate these from other tracers carried negligibly. Crude general rules have been formulated to explain this behavior, but little is known indeed about the factors involved. Certain trivalent hydroxides carry alkaline earths fairly well, for instance, and others do not carry appreciably. The carrying properties are dependent on the precipitation conditions and are diminished by increase in the concentration of the alkaline earth ion.

Another type of carrying is that based on the occurrence of isomorphism between compounds of the tracer substance and the carrier compound. If the system consists of substance A forming the compound A_nC and substance B forming the isomorphous compound B_nC the fraction a of A precipitated with fraction b of B, for complete equilibrium of precipitate and solution, is predicted to be:

$$\frac{a}{b} = \frac{(1-a)}{(1-b)} D \qquad (1)$$

under the assumption of ideal solutions or suitable correction thereto (Law of Nernst-Berthelot). D is a function of the solubility products of A_nC and B_nC and the departure from perfection

of the solid solutions. Where precipitation occurs rapidly, Doerner and Hoskins have predicted the relation:

$$\ln (1 - a) = D \ln (1 - b) \quad (2)$$

It appears to be difficult to realize experimental conditions for equation 1 to hold, particularly if the precipitates are but slightly soluble. The exploration of the distribution function under such conditions should, however, give useful information about the imperfection of the solid solution $A_xC = B_xC$ which can be correlated with ion size and other properties of the solid, although little has been done on this type of problem. More rapid precipitation does not generally lead to the distribution function of equation 2 with the same constant D as equation 1, and much more information is required in this direction. Very interesting experiments can be formulated if first substance A and then substance B is used at the tracer concentration level.

If the general laws of carrying become better understood, particularly in the field of isomorphous carrying, it seems reasonable that one can predict quantitatively the properties of compounds of elements available in tracer concentrations only, since the solubility and properties of ions in the solid state and in solution are a function of the charge, ionic radius, and polarizability. The successful solution of this problem would represent a major accomplishment in physical chemistry, and this problem is therefore a challenge to the chemist today.

Conclusion

The main purpose of this article has been to familiarize the chemist with the techniques and accomplishments of nuclear chemistry, and to show him how these techniques offer him avenues of approach to problems of his own. An effort has been made to show what problems are currently being attacked by chemists specializing in nuclear chemistry, and how the general chemist can contribute to these problems. There is a great need in the field for more correlation with conventional chemistry, and for the participation of more organic chemists, physical chemists, inorganic chemists, and chemical engineers in the efforts in nuclear chemistry, or in breaking down the barriers surrounding this field by taking some of the techniques into diverse fields.

Some of the problems mentioned above will have to be carried out in conjunction with a nuclear laboratory with pile or other production equipment, but the large majority of problems can be, and will be, carried out in the universities and industrial laboratories all over the world, as knowledge and appreciation of the field spreads. This spread cannot but help chemistry as a whole, and will have a most salutary effect on nuclear science.

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Radio-frequency Spectroscopy in Nuclear Studies

By ARTHUR ROBERTS

Department of Physics, State University of Iowa
Iowa City, Iowa

RECENT SPECTROSCOPIC APPLICATIONS of radio-frequency techniques in nuclear physics include nuclear radio-frequency resonance absorption and the exploration of the radio-frequency spectra of atoms and molecules in the newly accessible microwave region. The pioneer investigations of radio-frequency spectra were made with atomic and molecular beams by Rabi and his coworkers before the war. It now appears that the newly developed techniques will supplement the powerful molecular-beam methods.

Radio-frequency investigations of nuclear properties are aimed at discovering the static properties of nuclei. They have for their goal the measurement of both nuclear spin and nuclear moments—the magnetic dipole moment, electric quadrupole moment, and possibly higher moments that may exist. They can be applied also to the measurement of precise nuclear mass ratios and relative abundance of isotopes. It is thus possible that they will give rise to practical laboratory methods of chemical and isotopic analysis, in the same way that spectroscopy, X-rays, mass spectroscopy, and radioactive tracers have been used.

Radio-frequency spectroscopy gives, in addition, a wealth of information of interest to scientists other than nuclear physicists. It yields data on the interaction of nuclei with the lattice structure in liquids and solids; the interaction of molecules in a vapor or gas; the internal magnetic fields in molecules and lattices; the structure of atomic and molecular spectra; bond distances, moments of inertia, and other structural data concerning molecules; and, doubtlessly, other information of a nature not yet anticipated.

Radio-frequency investigations of nuclear properties fall into two quite distinct classes. One is called *nuclear induction* or nuclear radio-frequency resonance absorption; the other is called *microwave spectroscopy*, although it is by no means limited to microwaves.

Nuclear Induction

The discovery of nuclear induction was made independently by Purcell, Torrey and Pound (*1*), and by Bloch, Hansen, and Packard (*2*). The phenomenon had previously been unsuccessfully sought by Gorter and Broer (*3*). This failure, it now appears, was probably due to an unfortunate choice of sample in which the effect was looked for since, in some substances, for reasons still unexplained, absorption cannot be found.

Nuclear radio-frequency resonance absorption, in principle, is a simple phenomenon. When internal atomic and molecular magnetic fields vanish, as they do to a high approximation in almost all solids and liquids, the only remaining magnetic fields are those due to the magnetic dipole moments of the nuclei. Such fields are quite small. In a strong external magnetic field, the nuclei then align themselves with respect to the external field. If the nuclear spin is I, there are then, according to the familiar vector model of the atom, $2I + 1$ orientations possible, and thus $2I + 1$ distinct energy levels. These are equally separated, the energy difference between them being given by $E = \mu H/I$, with μH as the total energy of a magnetic dipole μ in a field H.

By the quantum condition, transitions between these states will have a frequency ν, given by $E = h\nu$. Now most nuclei have magnetic moments not exceeding one or two nuclear magnetons. Since the nuclear magneton, the

A report on a powerful new electronic technique for fundamental nuclear studies which may also result in practical methods for chemical and isotopic analysis. Basic physical concepts involved are discussed in detail, and types of unavailable electronic equipment currently needed are noted

unit of nuclear magnetic moments, has the value 5.049×10^{-24} ergs per gauss, it follows that most nuclear energy level separations in magnetic fields of the order of thousands of gausses will lie in the radio-frequency region. Then, if a system of nuclei in a strong magnetic field is irradiated by quanta of the appropriate frequency, resonance absorption can take place, precisely as resonance radiation can be absorbed in optical transitions in atoms.

Optical versus Radio-frequency Transitions

There are, however, some significant differences between ordinary optical transitions and radio-frequency transitions. One such difference concerns the method of detection. It is possible to use optical or infra-red methods in the radio-frequency region, and to measure absorption simply by recording the amount of energy transmitted as a function of frequency. This is sometimes done. In many cases, however, it is more convenient to use specific radio-frequency techniques, which may be extremely sensitive.

Another important difference arises from the fact that the energy of a radio-frequency transition is small compared to ordinary thermal agitation energy, whereas the energy of an optical transition is large. As a result, the population of the $2I + 1$ states, occupied by the nuclei in a magnetic field, will be almost identical, as contrasted with optical transitions in which the number of atoms normally in the upper state is negligible. The number N of atoms or molecules in a state of energy E above a ground state is given (except in some special cases where a nuclear statistical factor is introduced) by the Boltzmann relation $N = N_0 \exp(-E/kT)$, where N_0 is the number in the ground state, k is the Boltzmann constant and T is the absolute temperature. Both N and N_0 are subject to statistical fluctuation, which is small when the numbers are large. For an energy $h\nu$, corresponding to a frequency of 30 mc, N and N_0 differ by less than one part in 10^5 at room temperature.

The Boltzmann relation applies strictly only when thermal equilibrium has been established. In a system of atoms not subjected to an external magnetic field, all nuclei have the same average energy. When an external field is applied, equal numbers of atoms will at first populate each energy level, and some time will elapse before thermal equilibrium is established. This time, which is referred to as the *relaxation* time, depends upon the nature and strength of the interaction of the nuclei with their surroundings, since the excess energy must be carried away somehow. In contrast with excited optical states, which have natural lifetimes of the order of 10^{-8} seconds for spontaneous radiation, the natural lifetime of a level, whose energy is given in megacycles, is measured in thousands or millions of years. Clearly, some other mechanism for establishing thermal equilibrium must exist if it is to be attained.

The nature of the mechanism for shortening the relaxation time depends upon the properties of the excited states. The type of radiation emitted in a transition between adjacent energy levels of nuclei in an external magnetic field corresponds to a change in the component of the magnetic dipole moment along the direction of the field (or, in some cases, the electric quadrupole moment).

The lifetime of such a level is determined by the probability of spontaneous radiation, which is negligibly

small, and by induced radiation. Induced emission of magnetic dipole radiation is caused by the presence of magnetic fields which have Fourier components whose frequency corresponds to that of the transition. In the case of solids and liquids, the only naturally existing magnetic fields are those due to neighboring nuclei (except in paramagnetic and ferromagnetic materials). Since these nuclei are subject to thermal and molecular agitation, the magnetic field at any nucleus is subject to statistical fluctuations. The Fourier component of these fluctuations at the transition frequency is responsible for the small probability of induced emission and gives rise to an observable relaxation time. When electric quadrupole radiation is possible, similar arguments apply to the gradient of the electric field.

In the case of water at room temperature, the relaxation time is found to be of the order of seconds. In liquid, the relaxation time has been found to be related to the viscosity (*4*), so that viscous liquids have short relaxation times. In some solids, no resonances have been found; either they may be very broad, or the relaxation time may be very long.

Relaxation Time Changeable

The relaxation time can be changed by changing the viscosity of a liquid, or by introducing paramagnetic salts, so that the random fluctuations of the magnetic field are greatly increased. In addition, the presence of a strong, external, radio-frequency field in resonance with the transition frequency can broaden the resonance by greatly increasing induced-emission probability.

If a reasonably short relaxation time can be obtained, thermal equilibrium is attained at some time after the magnetic field has been established, and absorption thus becomes possible. The total power that can be absorbed is then determined by the size of the sample, the transition energy, and the relaxation time. For N atoms at temperature T, with nuclear spin I and relaxation time t, the power is $P = \frac{2I}{2I+1} \frac{N}{t} \frac{(h\nu)^2}{kT}$.

This quantity is of the order 10^{-9} watts for 1 gm of water at room temperature and for a frequency near 30 mc. To detect such an absorption, then, it is necessary to devise an apparatus in which a 30-mc magnetic field is applied to a sample of water.

Another effect, closely related to the absorption, is the one which gives rise to the name of nuclear induction. Consider the vector sum of the magnetic moments of all the nuclei in unit volume; this is the magnetic moment per unit volume, a vector we denote by **M**. Because of the very large number of atoms involved, it is legitimate to consider **M** from a purely classical, dynamic viewpoint.

Classically, in an external magnetic field, **M** will precess around the direction of the field with the Larmor frequency. In the presence of a radio-frequency magnetic field at or near resonance with the Larmor frequency and at right angles to the fixed magnetic field, the angle of precession of **M** around the fixed field will be increased. The precessing nuclei will then be capable of inducing a voltage in a coil suitably located around the sample (*5*).

Thus, if two coils are placed at right angles in the fixed field, and a sample placed inside them, a radio-frequency magnetic field from the first coil, the primary, will drive the magnetic nuclei in phase, like an armature, and the rotating magnets will, under suitable conditions, induce an observable voltage in the secondary coil. The plane of polarization of the total r-f field, which is the sum of the impressed field and the field due to precession, will be rotated, just as in the Faraday effect. It is this rotation which produces a component at right angles to the original field.

A complete analysis of what takes place is rather complicated because of relaxation time phenomena; however, Bloch (*6*) has shown that nuclear induction and nuclear absorption are closely related, and are, in fact, two aspects of the same phenomenon.

Four methods are now available for observing nuclear r-f absorption or induction. They employ, respectively, an r-f bridge, a special device which might be called a nuclear induction transformer, a superregenerative detector, and an autodyne detector.

The r-f bridge (*1*) is perhaps the most straightforward. In this method, nuclear absorption unbalances an r-f bridge, giving rise to a signal in a receiver used as a detector. In the Bloch method (*5*), the nuclear induction transformer is a device in which the establishment of nuclear resonance causes a change in coupling between the primary and secondary of a transformer, and thus a change in the output voltage. In the superregenerative method (*7*), a superregenerator is used both to establish nuclear resonance and to detect the induced voltage from it. In the autodyne method (*7, 8*), a weakly oscillating detector is modulated by the nuclear absorption.

The sensitivity of the bridge method is probably as high, if not higher, than that of any other detector. Purcell has shown (*9*) that 10^{19} atoms are detectable by this method, which uses a modulation technique that allows very narrow receiver bandwidths to be used.

The sensitivity depends in practice upon the width of the observed resonance, and increases until the instrumental width is less than the natural width. The natural width depends upon the substance used, and, in some liquids, is less than a thousandth of a gauss. In solids, much greater widths are often found (*10*). Accordingly, the homogeneity of the magnetic field is often a limiting factor in the sensitivity.

Applications of R-f Absorption

The most immediate application of nuclear absorption is to the measurement of nuclear gyromagnetic ratios, μ/I. These are obtained by measuring the frequency of absorption in a known magnetic field. Since absolute magnetic field measurements are difficult, gyromagnetic ratios (or magnetic moments, if the spins are known) are measured by comparison with a known magnetic moment in the same field (*11, 12, 13, 14*). The most accurately known magnetic moment is that of the proton, which is known from molecular beam work to a precision of one part in 3,000 (*15*). Absolute measurements are therefore limited to this precision, but relative measurements to one part in 100,000 have already been performed (*11*). Such relative measurements may be limited in precision only by the accuracy with which frequency can be measured.

Conversely, since the proton moment is known to one part in 3,000, magnetic fields can readily be measured to this precision. In addition, magnetic fields can be compared with a precision depending only upon the precision with which radio frequencies are measured. Changes of one part in 100,000 are readily detected, and the ultimate precision is usually limited by the homogeneity of the field, which determines the apparent width of the resonance.

Nuclear Spins Measurable

Nuclear spins can be measured, since the intensity of the signal obtained is a function of the spin (*6*). It is also a function of many other quantities, including relaxation time, line width, frequency, and so on, so that spin measurements in practice are likely to be somewhat difficult. The spin of H^2 has been determined by this method (*12*).

Since the intensity of the signal depends upon the number of nuclei present, nuclear r-f absorption is also applicable, in principle, to determinations of isotope ratios. The sample used in such measurement is not expended. As we have seen, 10^{19} atoms or thereabouts are required at present, although there is no theoretical reason why this quantity cannot be greatly decreased. It is clear that for such determinations careful control of the chemical composition of the sample, the magnetic field homogeneity, relaxation time, and power level are required, as well as knowledge of the nuclear spin.

Microwave techniques have been enormously improved as a result of

wartime advances, especially in the field of radar, making possible a great number of experiments which were formerly impractical. There are a large number of transitions between levels in atoms and molecules whose energies correspond to frequencies in the radio region. Such transitions are now being studied by r-f techniques. Since by far the greatest fraction of the accessible r-f spectrum lies in the microwave region, these techniques are generally referred to as microwave methods, even though they are equally applicable to lower frequencies.

Types of Transitions Accessible

There are several different types of transitions which are accessible to study by these methods. The hyperfine structure separation of atomic energy levels usually lies in the radio-frequency region; the fine structure of the hydrogen spectrum is also accessible (*16*). The ammonia molecule has a special type of spectrum, called the inversion spectrum, in the microwave region (*17*). The largest number of transitions in this region, however, are due to those transitions in the spectra of molecules which occur between rotational levels of a given vibrational state. Usually the ground vibrational state of the lowest electronic state is studied. For all but the lightest molecules, at least one such transition lies in the frequency region corresponding to wavelengths of one mm or more, and many transitions have wavelengths of 1 cm or more.

Just as in atomic spectra, nuclear interactions with the molecular fields give rise to a hyperfine structure (*17*). Also external magnetic and electric fields can be used to produce Zeeman- and Stark-effect splittings of spectral lines. In practice, the most important hyperfine splittings in the microwave region in molecular spectra are those due to the presence of a nuclear electric quadrupole moment, which may occur in any nucleus whose spin is greater than ½ (*18, 19*).

Since microwave spectroscopy uses gases or vapors, the experimental conditions are easier to interpret than those in nuclear r-f absorption experiments in liquids or solids. The relaxation time effects are quite different. While the natural line width due to spontaneous emission is still very small, emission can be induced by collisions, and the natural line width will depend upon the average time between collisions. This time, in turn, depends upon the gas pressure and the dimensions of the vessel containing the gas. Doppler broadening imposes another limit. Line widths of less than 100 kc can be obtained at frequencies near 25,000 mc at room temperature. The population difference between the levels involved in a transition is proportional to the frequency, and the overall absorption increases as the cube of the frequency. Thus, at high frequencies, a much bigger absorption effect per atom is observed, and more power can be used with the same number of atoms. In practice, the power limitation imposes no real difficulty.

Microwaves Simplify Detection

As a result of all these differences, we find that, while the detection of 10^{19} atoms becomes difficult with the nuclear r-f absorption methods, the detection of absorption by 10^{16} atoms or molecules is not difficult by microwave methods, and that this sensitivity shows every promise of being increased by several powers of ten. Indeed, the theoretical limit of sensitivity of narrow-band receivers is such that the detection of changes of received power of a few thousand quanta per second, at a 1-cm wavelength, is possible. With reasonable assumptions concerning line width and population, this allows in principle the detection of absorption by only 10^3 or 10^4 atoms.

The major interest of microwave spectroscopy to the nuclear physicist lies in the possibility of measuring some important nuclear properties. These include nuclear spin, magnetic moment, perhaps the electric quadrupole moment, relative isotopic abundance, and isotopic mass ratios. In the last two categories, it is as yet far from competing with the mass spectrometer.

As was pointed out earlier, microwave spectra also yield a wealth of other data not of specific nuclear interest. These include interatomic bond distances, moments of inertia, molecular electric dipole moments, centrifugal distortion and other structural data.

Methods Used

In microwave spectroscopy, an absorption cell (usually a waveguide) or a resonant cavity is filled with a gas or vapor at low pressure, and the absorption or dispersion is measured as a function of frequency. The measurement may be straightforward, as by filling the cell with gas and measuring transmitted energy as a function of frequency. More sophisticated methods are employed in order to increase the sensitivity and precision. Thus, variations in transmitted power, caused by frequency sensitivity of the r-f components, can be practically eliminated by using bridge methods or a modulation technique. In this manner, the radio frequency is held fixed and the absorption frequency of the gas varied by means of the Stark effect using an electric field.

One of the current major technical difficulties of microwave spectroscopy is a lack of oscillators covering the microwave region. Since only milliwatts or microwatts of r-f power are required, low-power oscillators (klystrons) are used, and these are currently available only for frequencies up to perhaps 10,000 mc and for the 24,000-mc band, plus or minus perhaps 10%. Harmonic generators have been used with available oscillators to reach other frequencies. Since sensitivity increases rapidly with frequency, and since absorption lines may occur anywhere, oscillators are needed for all frequencies that can be reached with known techniques. Crystal detectors, waveguide components, and accessories are also required. The design of these devices is well understood, and only engineering and production attention are required to make it possible to cover frequencies up to 100,000 mc or perhaps even higher.

Current techniques are adequate for observing lines from most molecules which are in the microwave region and are at accessible frequencies. (Difficulty will still be encountered with weak lines in the spectra of asymmetric rotors.) In some cases, even forbidden lines, whose intensities are quite low, have been observed; thus, the magnetic dipole transitions near 5 mm in oxygen (*20, 21, 22, 23*), and the hyperfine structure of the atomic spectrum of caesium near 3 cm (*24*), have been measured. The average rotational line has an absorption coefficient near 10^{-5} to 10^{-6} nepers per cm, and current techniques are able to detect absorption coefficients of 10^{-6} to 10^{-8}.

The Zeeman and Stark effects have a special application in microwave spectroscopy. They can, of course, be used in the traditional way, whereby the patterns produced by the application of a fixed external magnetic or electric field are analyzed to obtain information concerning the states involved. In addition, however, they can be used to modulate the gas absorption (*5, 24, 25*) and thus to permit the introduction of narrow-band modulation detection techniques which greatly increase the attainable sensitivity.

Operation of Modulation Method

A modulation method may work somewhat as follows: With an absorption line, the energy levels between which the transition occurs will be shifted and split by an electric field. If an undeviated line remains, its intensity will be much decreased. Now suppose a constant electric field to be switched on and off at some low audio-frequency rate. The change in absorption at resonance will then modulate the transmitted power at the audio frequency, and a tuned audio amplifier will detect the modulation. Both the original field-free absorption line or lines and the new pattern due to the applied field are modulated and can be detected.

Many variations of this procedure are possible. Hughes and Wilson (*25*) use a low radio frequency (10–80 kc) instead of an audio frequency. The Zeeman

effect, using a modulated magnetic field, is more convenient for atomic transitions (*24*), while the electric field is more convenient for molecular transitions. In the latter case, only a few hundred volts per cm are adequate to give large frequency shifts. In atomic transitions, magnetic fields of a few gausses are enough. Suitable electric fields have been obtained in a waveguide absorption cell by applying the voltage to a partition parallel to the broad face of the waveguide (*17, 26*). In a resonant cavity, the field is obtained by providing d-c insulation between parallel faces.

Applications to Nuclear Physics

The applicability of microwave spectroscopy to the study of a particular nucleus depends upon the possibility of obtaining the nucleus in question in the form of a monatomic gas in a state possessing a hyperfine structure, or as a constituent of a molecule which can be obtained as a gas. The gas must be obtained at a pressure of 10^{-2} or 10^{-3} mm, in quantities of the order of perhaps 10^{-7} mole (10^{16} atoms). Dilution by foreign atoms is inconvenient, but can be coped with up to reasonable limits—the rare isotopes S^{33} (*27*) and N^{15} (*25*) have been studied in their normal abundances of less than one percent. Greater dilution can be tolerated with improved techniques.

In the case of molecules, the molecule to be used must possess a permanent electric dipole moment to be most useful with current techniques; otherwise no rotational spectrum is allowed. Thus, as a rule, homonuclear diatomic molecules cannot be used. Their use requires techniques which will permit observation of forbidden spectra. Such techniques have been developed for special cases (*20, 22, 24*), and may perhaps be applicable in others. Finally, at least one spectral line must fall in an accessible portion of the radio spectrum.

If these conditions are met, it becomes possible to determine some important nuclear properties. Let us consider a favorable example, the molecule OCS, carbonyl sulphide. This is a linear molecule, possessing a permanent electric dipole moment, whose lowest rotational transition ($J = 0$ to $J = 1$) has a frequency near 12,000 mc. Other rotational transitions have frequencies which are almost exactly integral multiples of this frequency. This gas offers the opportunity for the study of the isotopes of carbon, oxygen, and sulphur.

Frequencies measured for various isotopic varieties of OCS for various transitions are tabulated below.

Frequencies of OCS Lines

Molecule	*Transition (J)*	*Frequency (mc)*	*Ref.*
$O^{16}C^{12}S^{32}$	$1 \rightarrow 2$	$24{,}325.92 \pm 0.02$	28, 29
	$3 \rightarrow 4$	48,651.7	29
	$4 \rightarrow 5$	60,814.1	29
$O^{16}C^{12}S^{34}$	$1 \rightarrow 2$	$23{,}731.33 \pm 0.03$	27, 28
	$3 \rightarrow 4$	47,462.3	29
$O^{16}C^{12}S^{33}$	$1 \rightarrow 2$	$24{,}020.3 \pm 0.1$	27
$O^{16}C^{13}S^{32}$	$1 \rightarrow 2$	$24{,}248.1 \pm 0.3$	27

All the lines of OCS studied so far have turned out to be single—they possess no hyperfine structure. This leads to the conclusion that either (a) none of the nuclei in question has a spin greater than ½ and thus possesses no electric quadrupole moment, or (b) if any nucleus has a quadrupole moment, the quadrupole interaction energy is too small to be observed. Therefore, either the quadrupole moment or the electric field gradient at the nucleus is extremely small. Experiment permits an upper limit to be placed on the possible quadrupole coupling energy. In the case of OCS, all isotopes of these elements whose spin is known have spins less than one. It can also be concluded that, in all probability, the spin of S^{33}, which has not been previously measured, is ½.

As a contrasting example, let us consider the microwave spectrum of the rotational transition $J = 1$ to $J = 2$ of the molecule ClCN, cyanogen chloride. In this case it is found that the spectrum of both isotopic varieties $Cl^{35}C^{12}N^{14}$ and $Cl^{37}C^{12}N^{14}$ show a wide splitting with

many components (*30*). The patterns of the splittings are such as to permit the unambiguous conclusion that the spin of each of the chlorine isotopes is $\frac{3}{2}$ (*31*), and not $\frac{5}{2}$, the value previously accepted from studies of band spectra. The pattern of lines of each isotopic variety covers nearly one hundred mc. In each case, the position the rotational line would have had in the absence of a quadrupole moment can be calculated. This is of interest for determining moments of inertia and bond distances.

The relative intensity of the two sets of lines gives the abundance of the corresponding molecular isotopic species. The frequencies, which can of course be measured extremely accurately, give a measure of the moment of inertia, and can be used to determine the mass ratio of isotopes of the same element (*27*).

In measuring relative abundance of isotopes, only rather small quantities of material are required. The samples used are not expended and can be recovered.

Microwaves Used for Light Elements

As yet, no practical applications of microwave spectroscopy to isotope analysis have been made. For light elements, such as H, C, N, O, S, Cl, etc., the method appears quite practical and suitable gases are known (OCS, NH_3, ClCN, CH_3Cl, etc.). Suitable gases or vapors may well be found for many other elements.

Other possibilities exist for independent microwave means of determining nuclear spin and statistics. One of these is the observation of alternation of intensities, in the manner traditionally used in band spectra. In molecules containing two or more identical atoms, characteristic variations of intensity due to nuclear statistical factors appear in the spectrum. Thus the microwave spectrum of ammonia shows intensity variations (*17*) which provide an additional demonstration of the fact that the proton has a spin of $\frac{1}{2}$ and obeys Fermi-Dirac statistics. This method is not too useful for the study of rare isotopes unless they can be obtained in rather high isotopic purity, since otherwise the concentration of molecules containing identical atoms will be too small.

The nuclear spins can also be obtained from the Stark or Zeeman patterns of spectral lines in the microwave region. The inference is particularly direct in the case of the Zeeman effect of atomic spectral lines (*24*), but is also useful in molecular spectra (*32, 33*).

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SEPARATION OF STABLE ISOTOPES

A review of separation methods and equipment, together with a discussion of relative advantages of stable and radioactive isotopes. Although much of United States know-how for large-scale separation still remains officially classified, this article illuminates the fundamental problems involved

By DAVID W. STEWART

Eastman Kodak Company, Rochester, New York*

SEPARATED STABLE isotopes are still in growing demand, despite the rapid advances that have been made in the preparation of radioactive "tracers" and their general availability for research in the United States. In many applications, the radioactive isotopes are more suitable, or indeed are the only ones of use, but in a wide field a choice exists between the two types with some advantages on each side; in other cases, only the stable isotopes are satisfactory.

The widest use of either type of isotope is in tracer experiments, where elements in compounds of interest are tagged and later identified in the products of a chemical or biological reaction. The use of isotopes to label substances entering complicated reactions and subsequently to detect particular reaction products derived from them depends upon the well-established fact that chemical reactions discriminate so slightly between molecules differing only in the mass of a particular atom that the course of the reaction is not affected. In special cases, as in hydrogen, where the percentage difference in mass between the isotope used as a label (either H^3 or H^2) and the normal, abundant variety is large, chemical reactions and biological processes may discriminate significantly between species. This possibility must be investigated in preliminary experiments and conditions adjusted to minimize the effect or corrections calculated to allow for it.

Factors affecting the choice between a stable and a radioactive tracer vary from what may be called simple convenience to fundamental questions as to a suitable half-life for the radioactive type, or the degree of dilution anticipated in the experiment. The relative weight of each consideration will vary with the type of experiment to be performed, with the particular element to be tagged, with the type of measuring equipment available, and with the experience of the investigator.

Choice of Tracers

The elements occurring most commonly in organic materials, especially in living tissues, are carbon, hydrogen, oxygen, and nitrogen, with sulfur, phosphorus, iodine and a few metallic elements, such as calcium and iron, occurring less frequently. In Table 1 are summarized the stable and radioactive isotopes of some of these elements. As may be judged from the table, little choice exists in the case of nitrogen and oxygen; the stable forms (N^{15} and O^{18}) must be used, since the half-lives of possible radioactive varieties are so short as to make any but very brief experiments impossible. Conversely, experience has shown that radioactive isotopes of elements, such as phosphorus, iron, and iodine, are so convenient to use that no attempt has been made to prepare their stable isotopes for use as tracers.

The elements for which a choice exists between the stable and radio-

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active forms are hydrogen, carbon, and sulfur. At present, the radioactive forms of the latter two (C^{14} and S^{35}) and the stable form of hydrogen (H^2) are probably the more commonly used because of somewhat greater availability. The C^{14} and S^{35} may also be favored because counting equipment for detecting and measuring the radioactivity is less expensive and simpler to use than the mass spectrometer which is generally required for work with stable isotopes. Both types of equipment, however, are available commercially. Unfortunately, the energy of the beta radiations emitted by H^3, C^{14},

TABLE 1

Stable and Radioactive Isotopes

Element	*Mass*	*Abundance (if stable)*	*Half-life (if radioactive)*	*Source (See below)*
HYDROGEN	1	99.98	.....	
	2	0.02	.....	(1)
	3	.....	31 years	(2)
CARBON	10	.....	8.8 sec.	
	11	.....	20.5 min.	
	12	98.9	.....	
	13	1.1	.....	(3)
	14	.....	5100 years	(4)
NITROGEN	13	.....	9.93 min.	
	14	99.62	.....	
	15	0.38	.....	(3)
	16	.....	8.0 sec.	
OXYGEN	15	.....	126 sec.	
	16	99.76	.....	
	17	0.04	.....	
	18	0.20	.....	(5)
	19	.....	31 sec.	
PHOSPHORUS	29	.....	4.6 sec.	
	30	.....	2.55 min.	
	31	100	.....	
	32	.....	14.30 days	(4)
SULFUR	31	.....	3.2 sec.	
	32	95.1	.....	
	33	0.74	.....	
	34	4.2	.....	
	35	.....	87.1 days	(4)
	36	0.016	.....	

(1) Distributed by Stuart Oxygen Co., San Francisco, Calif., on allocation by U. S. Atomic Energy Commission.
(2) Distribution (at low concentration) through Atomic Energy Commission being considered but not available at present. See reference (*3*), this paper.
(3) Research Laboratories, Eastman Kodak Company, Rochester, N. Y.
(4) Distributed by Isotopes Branch, U. S. Atomic Energy Commission, Oak Ridge, Tennessee.
(5) Small amounts at low concentration available on same basis as H^2 (see 1 above).

Data on abundances and half-lives from G. T. Seaborg, *Revs. Modern Phys.* **16**, 1 (1944).

and S^{35} is very low as compared to most of the other radioisotopes, so that special counting equipment and special techniques of measurement are required which reduce the advantages of the radioactive forms. Favoring the use of stable isotopes in certain experiments is the lack of radiation hazard, both to the system under investigation and to the investigators. On the other hand, radioactive tracers must be used for experiments where it is desired to detect the tracer in intact tissue, or at a distance, since the measurement of stable isotopes requires conversion of part of the test material to a gas (usually H_2, N_2, or SO_2) for analysis in the mass spectrometer.

One fundamental difference between stable and radioactive tracers appears in the extent to which each can be diluted in an experiment before the tracer is lost. "Heavy" isotopes occur naturally at a concentration which is essentially the same no matter what the source, and this abundance can be measured readily to within 1%. Thus, if the natural abundance of C^{13} is 1.06%, a sample of carbon tracer may be said to be lost when its measured abundance is below 1.07%. This excess concentration of 0.01% is reached when 100% C^{13} is diluted about 10,000-fold with ordinary carbon, and this represents the limiting dilution which can be tolerated.

If accuracy of the tracer data must be high, then either the maximum dilution must be reduced so that the value of the final excess concentration will be greater than 0.01%, or the precision of the mass spectrometer determination must be increased. With careful operation, isotopic analyses good to 0.1% have been reported, but natural variations in the abundance of the tracer isotope in starting materials and reagents will introduce further uncertainties which must be checked in each experiment.

When radioactive tracers are used, the limit of detection is said to be reached when the activity of the sample reaches the level of background counts. The latter may be due to contamination, cosmic rays, or the natural radioactivity of the substance being examined. With special precautions, it has been estimated that C^{14} (with an initial activity of 3×10^{11} disintegrations per minute per gram carbon) can be followed through a dilution of 10^{10}-fold. While such extreme dilutions are often desirable in exploratory work, where the distribution of the tracer in the products is unknown, or where only minimum amounts of the tracer compound can be administered at the start, the advantage is less important in quantitative studies where product compounds can be isolated and purified, or where larger amounts of the tracer can be used initially.

Another type of experiment which contributes increasingly to the demand for stable isotopes is that involving double labeling. In most applications of the tracer technique to complicated systems, the major effort is in synthesizing the starting compound containing the tracer, in carrying out the reaction —possibly involving a long period of animal feeding—and in recovering fractions of the product to be examined. The actual measurement of radioactivity, or the determination of an isotope ratio, is but a small part of the task. In such cases, it is desirable to make each experiment yield as much information as possible, and the usefulness of double-labeled compounds containing both a radioactive and a stable tracer atom of the same element becomes obvious. By this technique, two different chemical groups within the molecule can be followed independently, and, if desired, tracers for other elements can also be added.

One type of application of separated isotopes other than their use as tracers must be mentioned. Sometimes a particular stable isotope is desired because of its own inherent nuclear properties, for example, the use of separated boron of mass 10 in neutron-counting devices. Ordinary BF_3 gas, containing about 18% of $B^{10}F_3$, is used in neutron counters, since the B^{10} nucleus absorbs neutrons and emits alpha particles which can be detected by their ionizing effect. The efficiency of such counters

can obviously be increased by enriching the B^{10} content. The U.S. Atomic Energy Commission makes limited quantities of boron containing 96% B^{10} available for this purpose.

General Methods

When it became obvious in 1940 that it would be desirable to separate U^{235} in appreciable amounts and that large quantities of deuterium would be needed, a thorough review was made of all the methods that had been used previously on other elements, and much work followed on the most promising of these. A summary of the problem of separation is given by Smyth (*1*), as well as in articles by Urey (*2*).

In general, separation methods for isotopes depend on small differences in the average behavior of molecules which are isotopically different. Since each group, separately, will include molecules differing markedly from the average in kinetic or internal energy, it is to be expected that there will be considerable overlapping in the behavior expected from the two groups. This means that it will be difficult, if not impossible, to devise a separation method which will produce a large change in concentration of the desired isotope in a single process. One notable exception to this principle must be mentioned.

Electromagnetic Method

The electromagnetic method, as used in the mass spectrometer for the quantitative analysis of isotope mixtures, does not depend on the average behavior of molecules, but rather on the motion of individual gaseous ions when acted upon by electrostatic and electromagnetic fields. In a mass spectrometer, a collimated beam of gaseous ions, accelerated by an electric field, is deflected by the action of a magnetic field acting at right angles to the direction of motion of the ions. The degree of deflection is determined by the ratio, e/m, and, for singly charged ions, will vary inversely, in discrete steps, with the mass number of the particle ionized. Ions differing by one mass unit will therefore be separated in space by a distance depending upon the physical constants of the apparatus. If suitable collector slits and receivers are provided, a separation which is essentially complete can be achieved in one "pass." This method can be applied to nearly all of the elements, although it is simpler if volatile compounds are available from which the gaseous ions can be formed and if the collected product is a solid which is readily retained in the collector.

The chief disadvantage of the electromagnetic method for producing separated isotopes is that the quantity of material which can be processed in ordinary mass spectrometers is very small. The difficulties of securing large quantities of gaseous ions, of preventing space-charge effects from disturbing their paths in the instrument, and of obtaining sharp focusing without limiting too much the dimensions of the ion beam, all have been solved in the calutron used for the separation of U^{235}, but information is not available on details of the method nor on cost of the process per gram of material separated.

Statistical Methods

Of the many statistical methods which depend upon the average behavior of isotopic molecules, only three —thermal diffusion, electrolysis, and chemical exchange—are now in actual use for the preparation of tracers, while a fourth method—distillation—is also important enough to warrant detailed mention. Other methods, which include centrifugation, electromigration, and several modifications of diffusion, have been shown to work on a laboratory scale but have not been used to prepare any quantity of product.

Diffusion

In all of the statistical methods, the degree of separation attained in one application of the simple process may be defined by the equation

$$\alpha = \frac{n_1'/n_2'}{n_1/n_2}$$

where n_1 and n_2 are the relative numbers of atoms of the isotopes of mass

m_1 and m_2, in the mixture before processing, and n_1' and n_2' are the corresponding numbers after processing. The quantity α thus expresses the number of fold increase produced in a given isotope ratio. As an example of a simple process resulting in the separation of isotopes, the diffusion of two gases through a porous barrier may be considered. Here, α is related to the masses of the diffusing molecules by the equation

$$\alpha_i = (M_2/M_1)^{1/2}$$

where M_1 is the molecular weight of the lighter gas and M_2 is that of the heavier. This equation applies only to the enrichment of the initial fraction of gas, α_i, which diffuses without appreciable change in the composition of the residue. In actual practice, the residue becomes depleted in the lighter component and the over-all value of α decreases from the instantaneous value of the diffusion coefficient given by $(M_2/M_1)^{1/2}$.

If the masses of the methane molecules, $C^{12}H_4$ and $C^{13}H_4$, are substituted in the equation just given, α is found to have the ideal value of 1.031 and a practical value, if about half of the gas is diffused, of nearer 1.02. Thus, normal methane, containing 1.06% C^{13}, would be separated into two fractions having C^{13} contents of about 1.04% and 1.08%. This change is proportional to the value of $(\alpha - 1)$.

If the diffusion apparatus is of such a size that an initial volume of 22.4 liters, containing one mole of methane at atmospheric pressure, is reduced by one half in unit time, then the residual volume after diffusion, containing 0.5 mole at 1.08% C^{13}, would include an excess of C^{13} weighing 0.0012 grams [6 grams $\times$ (0.0108 − 0.0106)]. This quantity may be called the "production" or transport of the single diffusion cell per unit time. Factors affecting this transport rate are seen to be:

(1) the number of moles of normal material processed per unit time,
(2) the initial abundance of the desired isotope, and
(3) the value of the quantity, $(\alpha - 1)$.

If the product is desired at a concentration higher than 1.08%, then additional diffusion stages must be provided, each of which will again change the ratio by the factor, α. Since, in this subsequent processing, part of the initial transport of C^{13} will be carried into the "unwanted" fraction, a second series of units must be provided which will strip out the C^{13} so that only material depleted in the desired isotope will be discarded. It is readily seen that this multiplicity of units, with problems of balancing gas flows along the cascade, would be difficult to operate even if the "know-how" developed in the plants separating U^{235} by gaseous diffusion were completely available. For the practical separation of isotopes of lighter elements, other methods are better.

One modification of the diffusion process commonly employed for the laboratory separation of tracers, especially C^{13}, is the thermal diffusion method developed by Clusius and Dickel (*4*) and used in the United States by, among others, Nier (*5*) at Minnesota, Watson (*6*) at Yale, and Weinhouse, Grosse, and others (*7*) at the Houdry Process Corporation. In this process, diffusion of a lighter species of molecule takes place, not through a porous barrier, but through a layer of the gas mixture itself under the influence of a thermal gradient maintained between opposite walls of the container. In many gases, the lighter component tends to concentrate at the hot surface.

The thermal diffusion constant is not a simple function of the molecular weights, but takes into account the forces of attraction and repulsion between isotopic gas molecules and their interactions in the transfer of momentum upon collision. The theory of the process has been considered extensively by Furry, Jones, and Onsager (*8*, *9*, *10*), and by others. For polyatomic molecules which do not behave as hard spheres, the diffusion coefficient is difficult to predict and, experimentally, is found to be small so that multistage units are required for practical separation. Fortunately, for ease of operation, if the separating region is

made in the form of a water-jacketed vertical cylinder with a hot wire at the center, convection is set up so that gas moving in one direction is continuously enriched in one isotope by the preferential thermal diffusion which acts radially, while the counter-moving gas is depleted in that isotope. The process continues until back-diffusion along the tube mixes the gases as rapidly as they are separated. Steady operation of the apparatus described by Watson (*6*) is reported to yield about 7 milligrams of C^{13} per day at a concentration of 20%.

In the operation of a thermal diffusion column, as in all separation methods, the rate of accumulation of excess heavy isotope is slow enough so that it becomes desirable to reduce the amount of material held in the apparatus. If an ultimate concentration of 20% C^{13} is desired, and the transport is a fixed fraction of a gram of C^{13} per day, fewer days will be required to reach the 20% level if there is less material which must be enriched. For this reason, separating units are graduated in size, with the largest unit handling the most dilute material and the final stage made as small as possible. Since the starting concentration in each stage increases over the preceding one, the transport may be held the same with a smaller physical size since there is less unwanted material which must be handled. Coupling between the units may be done through heated and cooled parallel tubes which, by convection, maintain adjacent points at the same concentration. Power and cooling water requirements for this method are considerable, but offsetting these is the minimum of labor required.

Distillation

The process of distillation may be used to separate isotopes through the slight difference in vapor pressure which exists between pairs of compounds such as H_2O^{18}–H_2O^{16}, H_2O–D_2O, or H_2–HD. The distillation of liquid hydrogen by Urey, Brickwedde, and Murphy (*11*) resulted in the concentration of HD in the residue to an extent which first permitted the spectroscopic detection of deuterium. In the distillation of H_2O^{16}–H_2O^{18}, the separation factor, α, is given by the ratio of the vapor pressures of the two species—about 1.013 at 11° C. For the molecules, H_2 and HD (which differ in mass by 25%), the effect should be much larger, and it is found that α in this case has a value of 2.75. Because better methods are available for the separation of deuterium, distillation has been used principally for the preparation of O^{18} concentrates, although this is not being done commercially at present.

In distillation, the simple process factor can be multiplied by using efficient fractionation columns in which the gas phase moves upward through packing which favors rapid equilibration with the downward-moving liquid phase. At each "theoretical plate" along the length, the separation is repeated. If the desired isotope concentrates in the liquid phase, liquid near the bottom of the column will be richest and will be converted into vapor by boiling, while normal liquid will be added continuously at the top. Vapor leaving the top of the column will be discarded, because it is depleted to the extent of a single fractionation. Since vapor-pressure differences decrease at higher temperatures, the distillation is commonly carried out at reduced pressure. The low-temperature distillation of carbon monoxide has been suggested by Urey (*12*) as a possibility for the separation of O^{18}. In general, it is difficult to reduce liquid hold-up in distillations, so that long periods of steady reflux are required to bring the system to equilibrium. The method is suitable, however, for handling large quantities of material at relatively low cost.

Electrolysis

As an alternate to distillation, electrolysis has been frequently used to concentrate deuterium. In the electrolysis of water, it is found that the hydrogen released contains from one third to one sixth of the normal concentration of deuterium, with the residue, on continued electrolysis, becoming enriched. Possible explanations have received a

great deal of attention and include:

(1) different rates of transport of H^+ and D^+ ions to the electrode,
(2) different rates of discharge of H^+ and D^+,
(3) different rates of combination and liberation of H_2 and HD or D_2, or
(4) chemical exchange of HD with H_2O to favor the production of H_2 and HDO.

The importance of the first effect is doubtful since no hydrogen ions exist in KOH solution, yet the electrolytic separation remains when the solution is made alkaline. The contributions of (2) and (3) are not fully understood since the kinetics of discharge and liberation appear to depend on the nature of the electrode surface and on the conditions of the electrolysis. The last effect, which involves a chemical equilibrium, is an important one, almost sufficient to explain the observed separation in some cases, and will be discussed more fully in the paragraphs on chemical exchange. Prior to the war, deuterium produced by electrolysis was commercially available in purities above 99.9%. Attempts to separate the isotopes of other elements by this method have shown little promise.

Chemical Exchange

The chemical exchange process, which has been adapted on a semi-works scale to the separation of the nitrogen and carbon isotopes, and on a larger scale to the wartime production of deuterium depends upon the fact that the equilibrium constant for an exchange reaction between isotopic molecules differs from unity. This difference depends, in turn, upon small differences in the thermodynamic properties of the molecules identical except for the mass of one atom. If we write the equation

$$HD + H_2O \leftrightarrows H_2 + HDO,$$

an equilibrium constant (defined in the usual way as $k = [H_2][HDO]/[HD][H_2O]$) greater than unity indicates that, at equilibrium, the products on the right are favored, while if k is less than unity, those on the left predominate. In the example cited, it can be shown by calculation as well as experiment that the equilibrium constant at room temperature is about 3.7, which means that a concentration of D will take place in the water phase if hydrogen gas, containing deuterium, is brought into equilibrium with it. In order to reach equilibrium in this system at moderate temperatures, catalysts must be used, and it is in the development of suitable catalysts that the greatest advance was made in the wartime production of D_2O. Actually, according to Smyth (*1*), a combination of this catalyzed chemical exchange reaction with electrolysis and distillation in a single counter-current unit was found most efficient.

Unfortunately, the relatively large differences that exist between compounds of hydrogen and deuterium (owing to the large percentage difference in mass) do not extend to compounds containing carbon, nitrogen, or oxygen isotopes. Equilibrium constants (experimental) for some of the most useful exchange reactions are shown in Table 2.

In the simplest case, where each molecule reacting contains only one atom of the isotopic element (Equations 1–4), the chemical equilibrium constant is equal to the fractionation factor, α, defined earlier, and in the last example the value of α is readily derived from the value of k. The small differences between these values of k and unity result in almost no detectable effect at the end of a single equilibration; this justifies the assumption that in tracer experiments there will be no appreciable discrimination between the heavy and the normal atoms.

The method used to multiply the

TABLE 2

Chemical Exchange Reactions

(1) $N^{15}H_3 + N^{14}H_4^+ \rightleftarrows N^{14}H_3 + N^{15}H_4^+$	($k = 1.034$)
(2) $HC^{13}N + C^{12}N^- \rightleftarrows HC^{12}N + C^{13}N^-$	($k = 1.026$)
(3) $HC^{13}O_3^- + C^{12}O_3 \rightleftarrows HC^{12}O_3^- + C^{13}O_3$	($k = >1.014$)
(4) $S^{34}O_2 + HS^{32}O_3^- \rightleftarrows S^{32}O_2 + HS^{34}O_3^-$	($k = 1.019$)
(5) $\frac{1}{3}CO_3^{18} + H_2O^{16}$ (liq.) $\rightleftarrows \frac{1}{3}CO_3^{16} + H_2O^{18}$ (liq.)	($k = 1.046$)

small exchange effect in order to produce high concentrations of N^{15} and C^{13} was developed at Columbia University by Urey and co-workers (*13, 14*).

Fig. 1 is an outline of a three-stage apparatus which has been in operation since 1941 for the production of N^{15} in accordance with Equation 1, Table 2. The fractionating units are packed columns with dimensions as indicated. Raw material (saturated ammonium nitrate solution) enters the apparatus at the top, flows down through the packing, and is continually returned up from the bottom of each stage by conversion to ammonia gas. This refluxing reaction is carried out by the continuous addition of sodium hydroxide, with boiling in the stripping units shown. Since the value of k in Equation 1 is greater than unity, the $N^{15}H_3$ in the ascending gas exchanges with the $N^{14}H_4^+$ in the descending solution, so that the liquid reaching the bottom of each unit is enriched in N^{15} and the gas reaching the top is depleted. A portion of the enriched liquid from the bottom of the largest stage is used as feed material for the second stage, etc. The ammonia gas from the top of the smallest unit, while containing less N^{15} by the factor α than the feed material for this final stage, still contains more N^{15} than normal nitrogen, so that it is fed back into the bottom of the second unit. The ammonia gas which reaches the top of the largest unit contains less N^{15} than normal nitrogen (again by the factor α), so that it is discarded. Figures in parentheses on the diagram indicate approximately the relative rates of flow through the various parts of the apparatus. Despite the tapering size of the cascade, the hold-up is large enough to require steady operation for a period of six weeks before the equilibrium concentration shown at the bottom (corresponding to 81.5% N^{15}) is reached.

In the production of C^{13} by chemical exchange, both Equations 2 and 3 have been used. Since the exchange between carbon dioxide and bicarbonate ion is slow, this method requires a catalyst to reduce the length of column required; hence the hold-up and the time necessary to come to equilibrium. A suitable column packing with a catalytic effect on the exchange has been developed by Reid (*15*), and the effect has been further favored by the operation of the CO_2 exchange at elevated pressure. The alternate method, involving the exchange between hydrogen cyanide gas and an aqueous solution of sodium cyanide, has been found not to require a catalyst and to be favored by operation at pressures below one atmosphere. The worst complication in this method has proved to be the polymerization of HCN, which must be repressed by the use of inhibitors, such as Na_2S or Na_2SO_3.

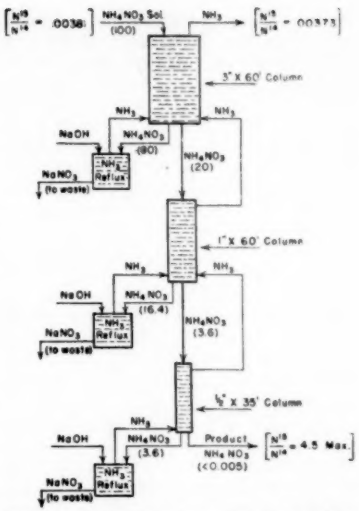

FIG. 1. Apparatus for concentrating N^{15}.

Fig. 2 outlines the apparatus now in use for concentrating C^{13} by the cyanide method. All parts in contact with enriched cyanide solutions have been made of glass, ceramics, or plastics to avoid the possibility of forming complex metallic cyanides which would not exchange further with HCN. In this process, the transfer of heavy carbon is preferentially into the gas phase, so that raw material starts at the bottom, as

HCN gas, and is enriched as it travels up to the top of each unit. At the top, the HCN gas is neutralized with NaOH solution supplied at a constant rate, and the NaCN returns to the bottom by gravity. The cascade is tapered to smaller sizes at the top in order to minimize hold-up. Since the apparatus operates under reduced pressure, leaks and dissolved air in the solutions contribute inert gas which must be removed at the top. This is done intermittently through a short absorber (not shown in the diagram) where all traces of enriched HCN are recovered and returned to the column. With this apparatus, equilibrium is reached in about two weeks and C^{13} may be withdrawn at concentrations up to 65%.

Equation 4 is illustrative of the chemical exchange method used to produce stable tracer sulfur (*16*). The apparatus and method of operation are exactly as shown for N^{15} in Fig. 1 except that sodium bisulfite solution is used instead of NH_4NO_3, sulfuric acid is added at the reflux units instead of NaOH, and the gas phase is sulfur dioxide instead of NH_3. Concentrations of S^{34} up to 25% can be produced with an apparatus of the size shown in Fig. 1. A concentration of S^{36} would also be effected in the process, but no quantity of this isotope has been prepared.

Chemical exchange methods for the concentration of O^{18} are still in the developmental stage. Equation 5 would allow the concentration of O^{18} in CO_2 gas brought to equilibrium with water. A catalyst of the type developed by Reid for the concentration of C^{13} would be required, and a method for the quantitative reduction of CO_2 to H_2O, with the return of the water to the column at the top, would also be needed. Another method which has been proposed is the similar exchange between SO_2[16] and H_2O^{18}. In this case, SO_2 would be converted to water at the top of the column by a reaction such as

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$$

Problems here include the possible formation of complex sulfur acids containing enriched oxygen, which might be lost at the top of the unit, and the removal of the precipitated sulfur in an anhydrous condition.

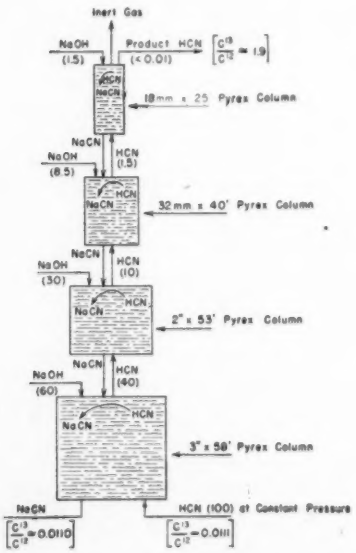

FIG. 2. Apparatus for concentrating C^{13}.

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Report on the Notre Dame Symposium on Radiation Chemistry and Photochemistry

THE FIRST SYMPOSIUM of its kind, the Radiation Chemistry and Photochemistry Symposium, held at the University of Notre Dame from June 24–27, brought research workers from the United States, Canada, and Great Britain in heavy attendance. Chairman of the conference was Dr. S. C. Lind of the University of Minnesota; Dr. Milton Burton of the University of Notre Dame acted as secretary.

Eighteen speakers contributed to the program; most of the papers presented are briefly summarized here.*

RADIATION CHEMISTRY

"Introduction to the Symposium." By DR. S. C. LIND, *Dean of the Institute of Technology, University of Minnesota.*

Even though radiation chemistry is not directly a part of nuclear chemistry, the two are closely related. High-speed neutrons act on the nuclei of the elements through which they pass, and in sharing their energy with light nuclei, they liberate high-velocity particles such as protons which are capable of producing chemical actions much like those produced by alpha particles.

It is of interest to learn what parts or particular radicals in large molecules are effective in absorbing the radiation and bringing about the observed changes. For example, if one considers a molecule containing one or more carboxyl groups, what can be predicted about the action of alpha radiation on the different radicals?

In liquid hydrocarbons bombarded by high-voltage cathode rays, it has been shown that abundance of methyl groups substituted for hydrogen in the straight-chain hydrocarbons increase the ratio of methane to hydrogen gas liberated. This is indication that, when ionization removes a bonding electron, the gaseous equivalent of the group disrupted is produced. Similar evidence has been determined for aliphatic acids of various chain lengths, particularly in the elimination of CO_2 and CH_4. It is more likely that the removal of CO_2 or other radical in such a manner would produce a molecular doubling, producing a di-carboxylic acid of double chain length rather than merely a condensation of the single molecular structure from which the radical was removed. Only by a complete quantitative examination of all the reaction products including the solid or liquid phase could it be determined whether such condensation takes place. Often a complete kinetic study of alpha-particle action is made difficult by the secondary action introduced.

There are two essential radiation chemistry theories. The first, that the ions themselves are direct agents in the reactions, has quantitative support but little theoretical support. The second, that radiation chemical effects are brought about by the action of free radicals or atoms, has little experimental but strong theoretical support. Practically nothing is known of the way the energy of alpha particles is expended except by ionization. The average energy expended per ion pair is about 35 ev and the ionization potential of most gases is about half this quantity; speculation is introduced as to the employment of the other half in bringing about action through intermediation of free radicals, atoms, or excited states. For example, about twenty molecules of acetylene polymerize to solid cuprene per ion pair. The reaction rate is proportional to the pressure and to the quantity of radon. But, if one of the inert gases is added to the acetylene, the rate of polymerization is increased and good kinetics are ob-

* The proceedings of the symposium including the complete texts of the papers presented, are reported in the current *Journal of Physical & Colloid Chemistry.*

tained only through the substitution for the partial pressure of acetylene the sum of its partial pressure and the equivalent (in terms of specific ionization) pressure of the inert gas. Reaction rate is proportional to the total ionization of both gases. The same yield is obtained with any of the inert gases.

"The Relation of Radiation Chemistry to Photochemistry" By DR. E. W. R. STEACIE, *Director, Division of Chemistry, National Research Council of Canada.*

Roughly half of the energy of a radioactive beam, it has been found, is expended in the production of ions, and the remainder in the produc i n of excited molecules. A photochemical reaction may be said to consist of three stages: (1) absorption of light leading to the formation of an excited molecule, (2) the excited molecule by decomposition or reaction giving rise to final products (these may be the final products or they may be atoms or radicals), and (3) secondary reactions of atoms or radicals. In many cases stage 2 follows stage 1 so rapidly that the result is kinetically the same as if absorption by radiation led directly to decomposition.

But in the case of radiochemical reaction the primary process leads both to ionization and to the formation of excited molecules. The importance of these excited molecules is still a matter under consideration. There has been much discussion concerning the mechanism by which the ions formed in the primary step lead to the chemical reactions which follow, whether they are mechanisms involving clusters or those involving ionic reactions. One reason for the clustering hypothesis' being strongly held by some is the polymerization of acetylene. It has been suggested, in the absence of obvious chain characteristics, that it is unlikely stepwise addition takes place and hence that the only alternative is a cluster of about 20 molecules of acetylene, which react on neutralization. In the first place this appears to strain the cluster idea rather severely. Secondly, it is now known that the polymerization of unsaturated hydrocarbons can be sensitized by free radicals; hence there is nothing against a mechanism involving step-wise addition as a result of the action of atoms or radicals.

Uncertainty about the excited molecule product stems from these sources. We know neither how many products are formed per ion, what properties they have, nor in how many different excited states they exist.

"Chemical Effects Accompanying Nuclear Decay by Beta Emission." By DR. T. H. DAVIES, *University of Chicago.*

Provided special perturbations from the nuclear process do not interfere, an increase in atomic number can be expected following the decay of a radioactive species by emission of nuclear electrons. Chemically excited species are produced; for example, two thirds of the Br^{83} produced from Se^{83} present in aqueous $SO_3^=$ is found in more reduced states than BrO_3^-. Suggested but not confirmed mechanism by which effects are produced are: (1) recoil processes which may lead to bond rupture or intramolecular rearrangement to products thermodynamically more stable, and (2) electronic excitation from the increase in nuclear charge.

Transformation of Organic Substances by Alpha Particles and Deuterons. By DR. IRVING A. BREGER, *Massachusetts Institute of Technology.*

Though high temperature and pressure were long thought of as sources of energy for petroleum formation, the temperature factor has been precluded and pressure has not been established. The possible role of radioactivity in petroleum genesis has long been considered, both radioactive elements in sedimentary rocks and decomposition and conversion of the solid and semi-solid organic compounds in source sediments having been suggested as radiation factors.

Fatty acids, identified previously in source sediments, were bombarded by alpha particles, which constitute 75 % of the energy liberated by terrestial radioactivity, and the isolation and identification of naturally occuring petroleum hydrocarbons resulted. Since intensity

of the alpha particles from radon was insufficient, the deuteron beam of the M.I.T. cyclotron was employed experimentally. The effects were similar, but larger quantities of conversion products resulted. In this way, a naphthenic acid, such as commonly found in crude oil, was irradiated and cyclohexane, also found in crude oil, obtained from it. Reactions which otherwise have been impossible may be investigated by use of these radiations. The production of hydrogen in laboratory radiation has been observed; its production is considered a problem. Natural gas contains traces of hydrogen; recent experiments have indicated that this hydrogen can be used in hydrogenation reactions under influence of radioactivity.

"Reactions of Bromine Atoms Produced by Isomeric Nuclear Transition by the Neutron-Gamma Reaction and by Light Absorption." By DR. JOHN E. WILLARD, *Professor of Chemistry, University of Wisconsin.*

Investigations of reactions of activated bromine with halegonated hydrocarbons such as CCl_4, CBr_4, C_2Cl_4, and $CHCl_3$ in the gas phase and in solution, are undertaken to gain information about the intermediate steps of chemical reactions. The bromine was activated in three ways: (1) by the neutron-gamma reaction which produces radioactively "tagged" bromine atoms with about 4000 Kcal/mol of energy, (2) by molecular nuclear isomeric transition which produces radioactively tagged positively charged bromine ions, (3) by light absorption which produces normal bromine atoms. The following points of evidence have been determined: (a) the nuclear process of neutron capture and isomeric transition, (b) the possibility of multiple bond rupture when an ion is neutralized with a polyatomic molecule acting as a third body to remove the energy of neutralization, (c) the "cage" effect by which solvent molecules prevent reactive molecular fragments from escaping from each other before reaction, (d) the possibilities of measuring more directly reactions involving atoms and free radicals in solution.

"Radiation Chemistry of Aqueous Solutions." By DR. A. O. ALLEN, *Director of Clinton Laboratories, Monsanto Chemical Company, Oak Ridge, Tennessee.*

To understand the effect of high-energy radiations on the human body with its high aqueous content, it is necessary first to understand the effects on water or substances that contain water. The effects of such rays on human bodies, in consideration of their possibilities of healing therapy or mass slaughter, are a matter of highest importance at the present time. Several observations are of noteworthy importance: Alpha rays, and some others, decompose water into hydrogen and oxygen, with some hydrogen peroxide formed; X-rays so used do not appear to decompose the water, but concentrate their effect on anything dissolved in it; "soft" beta rays, fast neutrons, and the fast ions produced by cyclotrons are intermediate in their effects. An explanation of these observations is made in that the free radicals are formed far apart by X-rays, and the hydrogen and peroxide formed are destroyed as fast as they are formed. The water does not appear to be decomposed, but the free radicals are able to act upon dissolved molecules. With alpha rays, the free radicals interreact. The amount of continuing decomposition is produced not only by many salts and acids but even by traces of dissolved glass formed in water when it remains in a glass container. The effects of traces of impurity makes the study of radiation effects in water very difficult. The whole problem reverts to the study of the free radicals themselves.

"Number and Spatial Distribution of Hydroxyl Radicals Produced in Water by Ionizing Radiation." By DR F. S. DAINTON, *Cambridge Univ., England.*

The primary radiochemical effect in water is in part ionization and in part excitation, with some unchanged radicals formed. Charge neutralization may produce more uncharged radicals. Radical recombination and absorption and dose rate affect the ionic yield magnitude. Liquid state compared with the vapor state shows increased ion

density, increased energy and probability of hydration of ions, deactivation of excited radicals, and immediate (Franck and Rabinowitch) recombination, including, of course, the possible kinetic consequences. Preliminary experiments have been made with X-rays, gamma rays, and hydrogen peroxide photosensitized polymerization of acrylonitrile and methacrylonitrile in dilute aqueous solution.

"Formation of Benzene in the Radiochemical Polymerization of Acetylene." By DR. CHARLES ROSENBLUM, *Merck & Co., Rahway, New Jersey.*

As much as 20% of gaseous acetylene polymerizing under alpha-particle influence may be converted to benzene, the yield of which drops during the reaction, presumably because of its subsequent polymerization. Since the acetylene polymerization ion yield is 21, two trimeric clusters would be necessary for every 26 acetylene molecules, but this is a contradiction of the basic cluster theory. Therefore, the preferred mechanism is a series of bimolecular addition reactions which at the trimer stage either cyclize to benzene or continue to form a high polymer. This later mechanism is favored by energy considerations.

"Radiation Chemistry of Geiger Counter Tubes." By PAUL B. WEISZ, *Socony-Vacuum Oil Co., Paulsboro, New Jersey.*

The "clicking" of a Geiger counter tube, used for the detection and measurement of nuclear radiations, is caused by the production of electrons within the tube concurrent with changes in the gas filling in the tube. The chemical effects within the tube are important in radiation chemistry, because they involve interactions between molecules, ion electrons, and light quanta in the far ultra-violet range. Molecular ion stability is a problem that may be answered by a study of the characteristics of Geiger tubes.

PHOTOCHEMISTRY

"Photochemistry of Ketones." By DR. W. ALBERT NOYES, JR., *President of the American Chemical Society and Head of the Department of Chemistry at the University of Rochester.*

The problem of the effect of light on various chemical substances is important in that eventually the sun will prove to be important as a source of energy. Light absorbed by chemical substances must be accounted for in one of three ways: heat, chemical energy to form new substances, or light energy as fluorescence or phosphorescence. The balance must be maintained. Molecules often split into fragments and the fragments join together to form new species. The fluorescence affords information on how molecules lose or gain energy during collisions.

"Metastable Ions." By DR. J. A. HIPPLE, *Head of the Nuclear Physics Division, National Bureau of Standards, Washington, D. C.*

A molecule struck by an electron having energy of 10–20 ev or higher may either lose an electron (ionization) or in addition split into various fragments (ionization and dissociation). This fragmentation is a reproducible phenomenon dependent only on the temperature of the molecules and the energy of the electrons. The mass spectrometer sorts these fragments according to their mass and relative intensity. In some molecules, the dissociation occurs at a detectable time interval after the ionization. This is observed in the spectrometer after the ion has been accelerated in the ion gun and before deflection by the magnetic field. The "lifetimes" of the various metastable states can thus be determined. A technique has been developed for determining the energy of the ions emerging from the exit slit of the mass spectrometer.

"Slow Electron Reactions." By DR. GEORGE GLOCKLER, *Department of Chemistry and Chemical Engineering, University of Iowa.*

The best example of photochemical reactions is the chlorophyl synthesis, but many other effects of radiation on chemical reactions are under study. To be able to understand, for example, the chemical reactions taking place in electric arcs and discharges, such as the

production of ozone and oxide of nitrogen during lightning discharge, the function of slow electrons in chemical reactions is of interest. These can be studied in radio-type tubes in which the gases are put at low pressure.

"Free Radical Determination with the Mass Spectrometer." By DR. GEORGE C. ELTENTON, *Shell Oil Company, Berkeley, California.*

In many chemical reactions, between the original and final products, there are formed intermediate products, sometimes called free radicals. These free radicals may be fragments of a molecule, or unstable complexes of atoms joined momentarily together. By free radical formation is meant chain reaction (not as in nuclear fission). Identification of radicals in such a reaction is difficult in most cases because of the short duration of their existence, sometimes $\frac{1}{1000}$ sec, and of their concentration, sometimes 0.001 %. With a mass spectrometer, identification of these free radicals was attempted by hitting them with electrons of carefully controlled velocity and converting them to moving charged radicals by knocking an electron off. These charged radicals can be bent in a magnetic field. Weight of the radical determines how much it bends around in its particular path. This is an aid in the determination of the radical construction.

"The Quenching of Fluorescence in Solutions." By DR. G. K. ROLLEFSON, *University of California.*

Experimentally valid tests show that the quenching of fluorescence is a second-order process competing with the first-order processes of the photo-activated molecule. Three processes are offered: (1) The quencher induces internal conversion of the excitation energy into thermal energy. (2) The quencher removes a relatively large quantity of energy by a specific transfer. (3) The activated molecule enters into some chemical reaction with the quencher, the net effect being reversed by subsequent dark reactions. Ionic quenching of dyes might be related to the second process mentioned.

"Reversible Photobleaching of Dyes and Pigments." By DR. ROBERT LIVINGSTON, *Professor of Physical Chemistry, University of Minnesota.*

The process of photosynthesis, consisting essentially of the production by a green plant in light of organic matter from carbon dioxide and water, is of great interest to the photochemist as well as the biologist. To study the steps in the process of photosynthesis which are characterized by the absorption of light energy (as quanta), it is necessary to study the fluorescence of chlorophyll and to study the reversible bleaching which chlorophyll solutions undergo when they are illuminated. Concerning reversible photobleaching: In purified solvents the extent of bleaching is proportional to the square root of light intensity. Oxygen inhibits it. Temperatures from 0 to 25° C have no noticeable effect on it. The effect of reducing agents is negligible, and oxidizing agents greatly increase it. Iodine at a concentration of 0.0005 % increases the bleaching about one hundred fold.

"An Interpretation of the Behavior of Some Organic Compounds." DR. MILTON BURTON, *Department of Chemistry, University of Notre Dame.*

The changing of organic compounds by high-energy radiation is influenced by the size of the bombing particle, the physical state and nature of the organic compound, and other factors. The low reactivity of benzene is attributed to its photochemical stability and the stability of the benzene ion itself.

"The Photochemistry of the Aldehydes." By DR. F. E. BLACET, *Professor of Chemistry, University of California at Los Angeles.*

A degree of correlation can be expected between the type of absorption which an aliphatic aldehyde exhibits at a given wave length and the chemical process or processes which follow absorption. Much work has been done on the photochemistry of acetaldehyde, taken as a typical example of aldehyde. Much time and effort can be saved if the primary process can be established earlier than done in the past.

Radioctivity Units and Standards*

In any expanding science, loose use of terms and values invites ambiguity. Here, collated for the National Research Council, is the standards manual on radioactivity

By ROBLEY D. EVANS
Massachusetts Institute of Technology

THE FOLLOWING MATERIAL was prepared for the use of the Subcommittee on Units in its report to the Committee on Nuclear Science of the National Research Council:

Electron volt. The electron volt (ev) and million electron volt (Mev) are units of energy.

1 ev = 1.60×10^{-12} ergs = 3.82×10^{-20} gram-calories
1 Mev = 10^6 ev
1 kev = 10^3 ev
1 atomic mass unit (amu) = 931 Mev/atom
m_0c^2 = 0.51 Mev (rest energy of the electron)
1 ion pair in air = 32.5 ev (Gray, 1936, 1944; Binks, 1936)

Curie. A curie is the quantity of radon (0.66 mm^3 at 0° C and 760 mm) in radioactive equilibrium with 1 gm of radium. The International Radium Standard Commission in 1930 (Curie, *et al.*, 1931) recommended extending the curie unit to include the equilibrium quantity of any decay product of radium, especially polonium. Thus "1 curie Po" is 2.24×10^{-4} gm of Po, or the amount which has the same rate of emission of alpha particles as 1 gm of radium. The Commission expressed its opposition to extension of the curie unit to radioactive substances outside the radium family.

The absolute disintegration† rate of radium has been the subject of many measurements by a number of methods, giving individual values between 3.40 and 3.72, with some indication in the more recent measurements that the true value probably lies in the neighborhood of $3.67 \pm 0.03 \times 10^{10}$ disintegrating atoms per sec per gm of radium. The Commission recommended use of the arbitrary value 3.7×10^{10} until the third figure is agreed upon.

Following discovery of artificial radioactivity, the curie unit came into widespread unofficial use as a statement of the quantity of any radioactive isotope. Thus, 1 millicurie (1 mc = 0.001 c) P^{32}, Na^{24}, or C^{14} meant the amount of the isotope necessary to provide 3.7×10^7 disintegrating atoms per sec. Then the number of atoms and the weight of isotope required to make 1 mc is inversely proportional to the radioactive decay constant λ or directly proportional to the half-period T, or to the mean-life τ ($\tau = 1.44T = 1/\lambda$). If n is the number of atoms and M the number of grams in

* These standards will appear in the important new book **"Advances in Medical Physics,"** to be published by Academic Press, Inc., New York. In Volume I of the book, they comprise the second part of a section entitled "Fundamentals of Radioactivity and Its Instrumentation."

† As used herein, the word "disintegration" connotes a spontaneous, measurably delayed transformation of a nucleus. Usually, but not always, a radioactive "disintegration" involves a spontaneous change in atomic number, Z. Thus, Z decreases by two units when an alpha ray is emitted by a nucleus; Z decreases by one unit when a positron beta ray is emitted, or when an orbital electron is captured by the nucleus; Z does not change in the isometric transitions, which involve only the emission of a gamma ray from the nucleus or of a conversion electron from the atom; and Z increases by one unit when a negative beta ray is emitted. Some workers (*e.g.*, Sizoo) have expressed the desire to replace the word "disintegration" by "mutation," especially for the many radioactive transformations in which the total number of nucleons does not change.

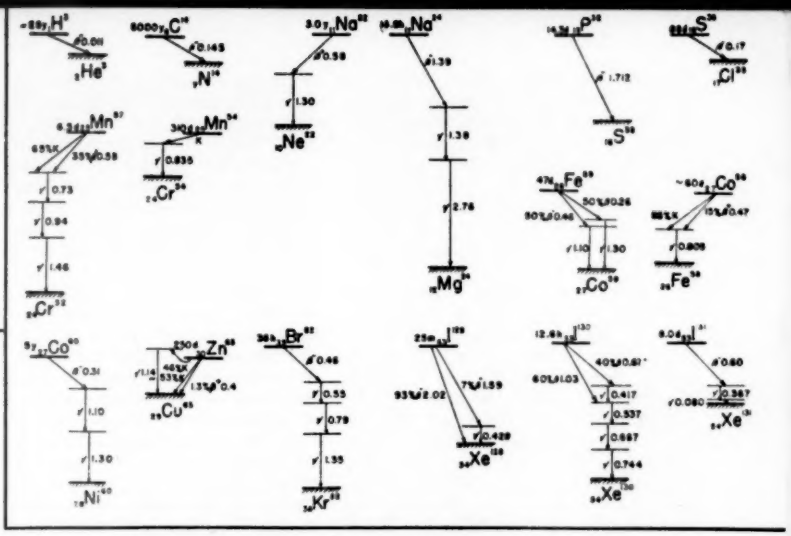

FIG. 1. Nuclear energy-level diagrams and disintegration schemes for some representative isotopes. Symbols: β^- = negative beta rays; β^+ = positron beta rays; K = orbital electron capture; γ = gamma ray. Internal-conversion transitions will be associated competitively with the gamma-ray transitions shown. The actual order of emission of cascade gamma rays is unknown in most cases. The numbers beside each transition show the energy of the gamma rays in Mev, or the maximum energy E_m of the continuous beta-ray spectrum, in Mev. The diagrams are to scale. Therefore the nuclear energy separation plotted for each beta-ray transition is the total energy of the disintegration (E_m + 0.51 Mev) = (maximum kinetic energy + rest energy) of the beta ray emitted. In electron-capture transitions, the final nuclear level may lie above the initial level, as in the 46% transition of Zn^{65}, because the reaction receives 0.51 Mev from the rest-energy of the captured electron. The nuclear energy change in the electron-capture disintegration of Mn^{54} is unknown, but is probably less than 0.51 Mev because no competing positron beta rays can be observed.

1 mc, N is Avagadro's number, and W is the atomic weight, then

$$n\lambda = 3.7 \times 10^7 \text{ sec}^{-1}$$
$$n = (M/W)N = 3.7 \times 10^7 \tau$$
$$M = 3.7 \times 10^7 \tau(W/N)$$

and 1 mc of P^{32} (T = 14.30 days = 12.35×10^5 sec), would contain:

$$n = (3.7 \times 10^7)(1.44 \times 12.35 \times 10^5) = 6.58 \times 10^{13} \text{ atoms of } P^{32}$$

or: $$M = (6.58 \times 10^{13}) \times \frac{32}{6.02 \times 10^{23}} = 3.5 \times 10^{-9} \text{ gm of } P^{32}.$$

Actually, the absolute rate of disintegration is exceedingly difficult to measure accurately for any isotope, especially all those which do not emit alpha rays. It is necessary to know the "disintegration scheme" of the isotope, that is, the beta- and gamma-ray spectrum, and the relative abundance and energy of all radiations emitted. At the beginning of 1947, the disintegration schemes of only about two dozen artificially radioactive isotopes were established with certainty. Representative examples are given in Fig. 1. When it is known that each disintegrating atom gives say one beta ray, and calibrated beta-ray counters (*e.g.*, Peacock, 1944) are available, an estimate of absolute activity of the sample can be made. If conversion electrons are present, their abundance and energy must be known, and corrections made.

If some of the transitions are by electron-capture, instead of by beta-ray emission, then 1 mc will emit less than 3.7×10^7 beta rays per sec. For

example, the 6.5-day Mn^{52} decays by positron beta-ray emission in 35% of the transitions, and by electron-capture in 65% of the transitions; therefore, 1 mc of Mn^{52} emits only $0.35 \times 3.7 \times 10^7 = 1.3 \times 10^7$ beta rays per sec. The curie unit has been misused occasionally to denote 3.7×10^{10} beta rays per sec instead of 3.7×10^{10} disintegrations per sec.

A much more serious misuse of the curie unit has been as an ambiguous unit of gamma radiation. This has arisen from radiological use of radon, whose absolute disintegration rate is properly measured in curie units. Radon gives rise to the decay products RaB and RaC whose complex gamma radiations (Fig. 2) have long been used in radiological practice. Many laboratories have misused the curie unit to describe any radioactive source which produces the same gamma-ray response as 1 curie of radon. An outstanding

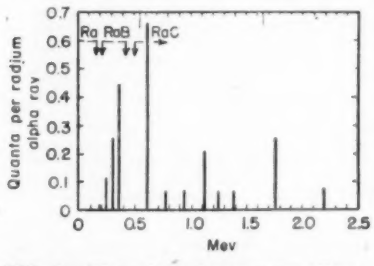

FIG. 2. The principal gamma-ray lines of radium and its equilibrium decay products. Radium itself emits only a low-energy gamma-ray of 0.184 million electron volts (Mev) and then only in 1.2% of the disintegrations, 98.8% of the radium alpha rays being unaccompanied by any gamma radiation. The decay product, radium B, emits beta rays and three important but low-energy gamma rays. Radium C emits beta rays and eight important gamma rays having energies as high as 2.2 Mev. On the average, each atom which decays through all the stages shown in Table 1 will have emitted 2.3 quanta of gamma radiation. References: Ellis and Aston, 1930; Gray, 1937; Ellis, 1933; Sizoo and Willemsen, 1938. Significantly different results for the relative intensity and energies of the lines in RaC at energies greater than 1.1 Mev have been reported by Latyshev et al., 1940.

technical objection to this practice is that the gamma-ray response depends profoundly on the detection instrument used. For example the ratio of the apparent gamma-ray intensity of a source of 8-day I^{131} to a source of radium (or of radon) is four times as great if a platinum cathode counter is used for both measurements as if a copper cathode counter is used with the same sources, geometry, and filtering. Moreover many isotopes emit no gamma rays at all, *e.g.*, C^{14}, P^{32}, S^{35}. An educational effort should be made by everyone to eliminate the conflicting and irrational use of the curie as a unit of gamma-ray source intensity.

In the meantime, caution is advised in interpreting the meaning of curie (c), millicurie (mc), and microcurie (μc) in the past and current literature. Even when the reader can assure himself that "curie" is used in the sense of disintegrating atoms per sec, he must ascertain whether the number 3.7×10^{10} or some other popular contender, especially 3.47×10^{10}, has been the author's intent.

Rutherford. In view of the justifiable position held by the International Radium Standard Commission that the curie unit be used only for radium (1 gm Ra = 1 curie), radon, polonium and other members of the radium series, a carefully defined new unit, the rutherford (rd), has been proposed for general use. Ambiguities as a result of choice of numerical values, failure to distinguish between beta rays per sec and disintegrations per sec, and extensions to arbitrary and undefined gamma-ray intensities, can then be avoided. With advice and concurrence of a number of interested individual physicists and laboratory groups, especially in the United States, Great Britain, and France, the National Bureau of Standards and the Committee on Radioactive Standards of the National Research Council have proposed (Condon and Curtiss, 1946) that the amount of any radioactive isotope which disintegrates at the rate of 10^6 disintegrations per sec be called 1 rutherford, abbreviated rd,

to distinguish between it and the roentgen (r). Thus:

1 rd = 1.00×10^6 disintegrations/sec
1 rd = $\frac{1}{37}$ mc of Ra, Rn, Po, etc.

The prefixes, "mega" (1 Mrd = 10^6 rd), "kilo" (1 krd = 10^3 rd), "milli" (1 mrd = 10^{-3} rd), and "micro" (1 μrd = 10^{-6} rd), may be used where needed, but in contrast with the curie unit the major part of the laboratory use of radioactive isotopes will need no such prefixes. Thus the therapeutic dose of P^{32} is of the order of 100 rd, while tracer doses of radioactive isotopes for biological studies and the amounts of many isotopes used in studies in nuclear physics are normally in the domain of 0.1 to 10 rd. The weakest sources which can normally be measured conveniently with Geiger-Müller counters are in the domain of 1 μrd (60 disintegrations per minute).

Roentgen. The roentgen was originally developed as a unit of radiological dose. Workers in physics and radiobiology have made use of the roentgen and a number of units derived from it.

The roentgen unit (r), as redefined at the Radiological Congress at Chicago in 1937, is "that quantity of X- or gamma-radiation such that the associated corpuscular emission per 0.001293 gm of air produces, in air, ions carrying 1 electrostatic unit of quantity of electricity of either sign."

The mass of air referred to is 1 cc of dry air at 0° C and 760 mm Hg. One electrostatic unit is $1/(3 \times 10^9)$ coulombs, or $1/(4.80 \times 10^{-10}) = 2.083 \times 10^9$ ion pairs. Therefore 1 r produces $2.083 \times 10^9/0.001293 = 1.61 \times 10^{12}$ ion pairs per gm of air. If an average of 32.5 ev is expended (Gray, 1936, 1944; Binks, 1936) to form each ion pair in air, then 1 r corresponds to the absorption of 5.24×10^{13} ev of energy (or 5.24×10^{13} ev $\times$ 1.60×10^{-12} erg/ev = 83.8 ergs) per gm of air. This ionization is produced by the secondary electrons [photo- (τ), Compton- (σ_a), and pair- (κ)] produced in 1 gm of standard air. Of course, the relative proportion of photo-, Compton-, and pair-electrons will vary with the energy of the gamma radiation.

Correct use of the roentgen as a unit of "quantity of gamma radiation" requires us to realize that the term "quantity" is used here in its common or household sense of "amount," and does not connote any exact physical magnitude involving the energy per photon, or the total number of photons, or the total energy of the beam of photons. Indeed, the roentgen does not involve any precise physical information at all about the quality (energy per photon) or intensity (energy flowing through unit area in unit time) of the gamma radiation. The "quantity" to which the roentgen really refers with physical exactness is the *"quantity of ionization"* produced in air by the secondary electrons formed in gamma-ray collisions with air molecules. Thus the roentgen is a unit of energy dissipation, by gamma rays or X-rays, in a standard arbitrary material, air. A schematic representation of the roentgen unit is shown in Fig. 3.

The roentgen does not depend on the *time* required for the production of the

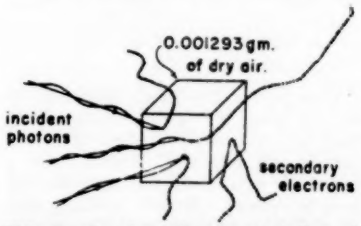

FIG. 3. A schematic representation of the roentgen unit of photon energy dissipation. Photons, of any energy, are incident from any directions, over any time interval. Even if the photons are collimated, the cross-sectional area of the beam is unspecified. The absorption of these photons in 0.001293 gm of dry air (1.000 cc at 0 C, 760 mm; 1.073 cc at 20 C, 760 mm), produces secondary electrons which, if completely absorbed in air, would produce a total ionization of 1 electrostatic unit of charge (1 statcoulomb), that is $1/4.80 \times 10^{-10}$ or 2.083×10^9 ion pairs. This ionization would be distributed along the relatively long individual paths of the secondary electrons.

ionization. Consequently gamma-ray *dosage rates* are represented in terms of roentgens per unit time. For example, an unvarying dosage rate of 12.5 mr per hr, if continued for 8 hours, would give a total dose of 100 mr, or 0.1 r. The maximum permissible daily dose for laboratory personnel exposed to gamma radiation over the entire body, is commonly taken in the United States as 100 mr in a 24-hour day (Burnam, 1938; Cantril, 1946). Again, an ionization rate of 1 ion pair per cm^3 of standard air per sec is $(1/2.08) \times 10^{-9}$ r per sec or 1.73 microroentgens (μr) per hour. The cosmic radiation produces about 2.4 ion pairs per cm^3 of standard air per sec at sea level, or 0.10 mr per 24-hr day. The cosmic and local gamma radiation at sea level is usually equal to or greater than 0.2 mr per 24 hr.

In summary, the official 1937 definition of the roentgen, when combined with current values of physical constants, leads to the following equivalent quantities:

1 r = 1 esu/cc std air
= 2.083×10^9 ion pairs/cc std air
= 1.61×10^{12} ion pairs/gm air
= 6.77×10^4 Mev/cc std air
= 5.24×10^7 Mev/gm air
= 83.8 erg/gm air.

Gamma-ray intensity. The unit of dosage rate, r per sec, is often loosely used in the older literature as a unit of gamma-ray intensity. Really, the r per sec is a unit of *ionization intensity* in a particular reference medium, dry air at 0° C and one atmosphere pressure.

True *gamma-ray intensity* is the rate at which photon energy flows past any point (or small region). True gamma-ray intensity can be expressed only in absolute units such as ergs per cm^2-sec, or as Mev per cm^2-sec. The ionizing effects depend not merely on the true intensity, but on the number and energy of the photons involved. Thus if 1000 photons per cm^2-sec, each of 1 Mev quantum energy, traverse an area of 1 cm^2, the gamma-ray intensity at this surface is 1000 Mev per cm^2-sec. The same intensity would be given by 500 photons per cm^2-sec, each of 2 Mev quantum energy. The Compton absorption coefficient, σ_a, for 1 Mev photons is 3.60×10^{-5} per cm in standard air. Similarly, for 2 Mev, the linear Compton absorption coefficient, σ_a, is 3.00×10^{-5} per cm in air. For air (average atomic number Z = 7.22), photoelectric and pair production absorption will be negligible at these energies. Consequently, the energy absorbed per cm of travel in air, or per cm^3 of air, for these two photon beams of equal gamma-ray intensity will be:

For 1 Mev:
$1000 \times 1 \times 3.6 \times 10^{-5}$
$= 0.036$ Mev/cm^3-sec
For 2 Mev:
$500 \times 2 \times 3.0 \times 10^{-5}$
$= 0.030$ Mev/cm^3-sec

Now if 1 r is $(2.083 \times 10^9$ ion pairs/$cm^3) \times (32.5$ ev/ion pair$) = 6.77 \times 10^4$ Mev/cm^3, the dosage rates or *ionization intensities* produced by these two beams of equal *gamma-ray intensity* will be:

For 1 Mev:
$0.036/6.77 \times 10^4$
$= 5.3 \times 10^{-7}$ r/sec
For 2 Mev:
$0.030/6.77 \times 10^4$
$= 4.4 \times 10^{-7}$ r/sec

We see that r per sec is not a measure of gamma-ray intensity but is instead proportional to the resulting *ionization intensity in standard air*. Thus r per sec is a rate of energy dissipation, not of energy incidence.

"Air-wall" r chambers. In the example just considered, some of the Compton electrons will have initial kinetic energies of the order of 0.7 to 1.7 Mev, hence ranges of as much as 0.3 to 0.8 gm per cm^2, or 2 to 6 meters of air. Yet the definition of the roentgen requires that we measure the total ionization produced by all the secondary electrons formed per cm^3 of standard air. To avoid large and cumbersome apparatus, small "air-wall" ionization chambers, or "thimble chambers," (*e.g.*, Wilson, 1945) have been developed. These follow

the general physical principles (Bragg, 1912; Fricke and Glasser, 1925; Gray, 1928, 1936) governing the ionization produced in a small cavity (*e.g.*, air) in a large mass of absorbing material traversed by gamma rays. When a tiny cavity, such as a small ionization chamber, is introduced into a large homogenous absorbing medium which is uniformly irradiated, the atmosphere of secondary electrons traversing the cavity is identical in every respect with the electron atmosphere which existed in the medium before the cavity was introduced. The cavity must be small compared with the range of the secondary electrons in the gas with which the cavity is filled (Gray, 1936; Sievert, 1940).

In a series of careful experiments, Gray (1936) has verified this principle, according to which the ionization, J, in ion pairs per cm³-sec in a small air cavity is given by

$$J = \Delta E / W\rho$$

where ΔE is the gamma-ray energy absorbed in the medium in ev per cm³-sec; W is the average energy expended per ion pair formed in the gas (W = 32.5 ev for air); and ρ is the stopping power of the medium relative to that of the gas for the secondary electrons, that is, an electron will lose the same energy in traveling Δ x cm in the medium, or $\rho\Delta$ x cm in the gas of the cavity. The average energy per ion pair, W, varies only slightly (Binks, 1936) with the electron's velocity, because swift electrons tend to transfer an important portion (perhaps 10 to 60 kev) of their energy to each atomic electron which they strike in an ionizing collision, and the average energy loss per ion pair is always characteristic of the less violent ionizing collisions by these slower secondary electrons. The relative stopping power, ρ, is almost independent of the electron's velocity, but decreases slowly with atomic number Z. In agreement with theory, Gray found ρ to be proportional to the relative electron densities NZ of the medium and the gas, except for the expected small decrease in ρ with increasing Z. This decrease amounts to about 9% between $Z = 6$ (C) and $Z = 13$ (Al), and an additional 8% between $Z = 13$ (Al) and $Z = 29$ (Cu). Thus in a set of thimble chambers, the ions per cc of air filling will increase slightly, with increasing Z of the wall materials. Taking the average atomic number of air as $Z = 7.22$, an error of less than 5% is made by regarding ρ as simply the ratio of the densities (gm per cm³) of the medium and the cavity gas, provided the medium is composed of light elements between $Z = 6$ and 13.

The thickness of medium necessary to validate the cavity-ionization principle is small. It is only required that the medium be thick enough to establish equilibrium between the primary photons and their secondary electrons, that is, about as thick as the maximum range of the secondary electrons in the medium. As this is only of the order of a few mm in media such as graphite, bakelite, Tenite II (Eastman cellulose acetate butyrate), Aerion (bakelite and graphite composition), or aluminum, one can simply employ a small air-filled ionization chamber having walls a few mm thick as both the cavity and the medium. Fig. 4 shows the effect of wall thickness on the ionization produced in a small graphite chamber filled with air and irradiated with gamma rays from RaB + C. Actually the wall of an "air-wall"

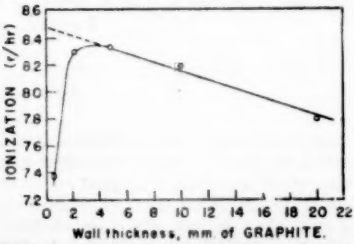

FIG. 4. Variation of ionization, due to a constant source of gamma rays, with wall thickness, for a small graphite chamber filled with air. A wall thickness of *ca.* 4 mm is required to produce effective equilibrium between the gamma rays and their secondary electrons. For thicker walls, the attenuation of the gamma rays by the walls is noticeable. (Mayneord and Roberts, 1937).

chamber can be somewhat thinner than the maximum range of the secondary electrons, because most of the ionization is produced by electrons formed in the inner few mm of wall material. It is to be noted, also, that the walls of the chamber should be thick enough to prevent secondary electrons from the surroundings, from filters, etc., as well as any beta rays from the gamma-ray source, from reaching the sensitive volume of the chamber.

The ionization (ion pairs per cm^3) then, in a satisfactory "air-walled" ionization chamber, should be:

(1) independent of the volume of the chamber
(2) proportional to the density of the gas in chamber
(3) proportional to the gamma-ray energy absorbed per cc of wall material
(4) inversely proportional to the stopping power of the walls for electrons.

If the chamber gas is air, and if the walls are composed of materials having an atomic number Z near that of air, then the ionization per gm of air in the chamber will be substantially the same as the gamma-ray energy loss per gm of air at the point where the chamber is located.

In an ideal thimble chamber, and if all ions formed are collected:

$$1 \text{ r/sec} = 1/(3 \times 10^9) \text{ coulombs/sec} \cdot \text{cc std air} = 3.33 \times 10^{-10} \text{ amps/cc}$$

and:

$$1 \text{ r/hr} = 0.926 \times 10^{-13} \text{ amps/cc std air.}$$

Roentgen-equivalent-physical, (rep). We have seen that the roentgen is a unit of photon energy dissipation in an arbitrary material, air, where 1 r is about 83 ergs per gm. In contemporary radiobiology, ionization in tissues is often produced by radiations other than photons. There is good evidence that the biological effects of various ionizing radiations depend, among other things, on the density of ionization (specific ionization) produced along the path of the particle in tissue. Thus a different degree of tissue damage can be expected from the absorption of 1 Mev of alpha-ray energy than from 1 Mev of beta-ray energy. Moreover the relative effectiveness will, in general, vary from one species of organism to another.

The roentgen has come to have a clinical interpretation because so many observations in terms of roentgens have been made of the effects of X-rays and gamma rays on tissues. When tissue ionization is produced by any primary radiation other than photons, (*e.g.*, beta rays, protons, alpha rays, neutrons) the doses may not be expressed in roentgens.

Then if the energy lost by ionization in the tissues is the same as the energy loss for one roentgen of gamma radiation absorbed in air, the dose is spoken of as one roentgen-equivalent-physical* (abbreviated "rep"). For example if one gm of tissue absorbs 10^8 beta rays having an average energy of 0.52 Mev, the total energy absorbed would be 52×10^6 Mev per gm, or 83 ergs per gm, or 1 rep. Then

$$1 \text{ rep} = 83 \text{ ergs/gm tissue.}$$

It is to be noted that 1 r of photons, which produces about 83.8 erg per gm of *air*, will produce a somewhat different energy dissipation in various tissues, because of the differences in chemical composition. The number of ergs per gm of tissue per roentgen varies (Spiers, 1946; Lea, 1947) with tissue composition and photon energy approximately as follows:

	825 *kev*	124 *kev*	12 *kev*
Muscle (Spiers)	95	94	87
Fat (Spiers)	89	84	42
Bone (Spiers)	157	245	883
"*Wet tissue*" (Lea)	92	91	86

The somewhat conventional statement that 1 r of photons = 1 rep is therefore an approximation.

Other units for the tissue doses delivered by various types of radiation include the *gram-roentgen* (Mayneord, 1940) which is the energy dissipated by gamma rays in 1 gm of air, *i.e.*:

* The *rep* and *rem* units were introduced by Dr. H. M. Parker.

1 gram-roentgen = 83.8 ergs in an unspecified amount of tissue, thus:

1 rep = 1 gram-roentgen per gm of tissue.

Gray and associates (Gray, *et al.*, 1940) in considering the energy dissipated in tissue by fast neutrons, have used an "energy-unit" defined as the same energy in 1 gm of tissue as is dissipated by gamma rays in 1 gm of water, which is about 93 ergs. Thus:

1 "energy-unit" = 93 ergs per gm of tissue.

The n unit, for fast neutrons. Availability of commercial "air-wall" thimble chambers, designed for the measurement of gamma-ray and X-ray dose, made their use convenient when it later became necessary to undertake the measurement of radiation doses from fast neutrons. Extensive theoretical and experimental studies have been made of the response of small ionization chambers to fast neutrons (*e.g.*, Gray and Read, 1939; Gray, 1944; Aebersold and Anslow, 1946). Material which is rich in hydrogen is especially effective in absorbing energy from fast neutrons, by the production of energetic recoil protons. The ionization produced in air-filled thimble chambers, relative to the ionization produced in tissue, therefore depends strongly on the hydrogen content of the walls of the thimble chamber. There is now general agreement that less ionization is produced in the Victoreen 100-r bakelite-walled thimble chamber than in tissue by a given beam of fast neutrons. When this size thimble chamber exhibits 1 esu per cc of standard air (*i.e.*, 1 r) of ionization due to fast neutrons, the dose is often called 1 n. That is, 1 n produces the same ionization in the Victoreen 100-r thimble chamber as would 1 r of gamma rays. However, the ionization produced in tissue by the fast neutrons is found by various workers to be between 2 and 2.5 times the ionization in the chamber. That is:

1 n = 2 to 2.5 rep $\simeq$ 190 ergs per gm of tissue.

Roentgen-equivalent-man (or mammal), (rem). The relative biological effectiveness (RBE) of ionization due to secondary recoil nuclei produced in tissue by fast neutrons, and an equal amount of tissue ionization due to gamma rays, has been the subject of many experimental studies on various species of micro-organisms, viruses, plants, and animals. Values of RBE between 0.5 and 20 have been observed among the wide variety of biological materials studied thus far. When any one particular biological reaction has been compared in several species of mammals, the reported RBE values have exhibited species variations of less than a factor of two. As measured for various radiation effects (acute mean-lethal-dose, shortening of life by chronic irradiation, blood counts, etc.) in mice, the secondary ionization produced by fast neutrons (about 2 Mev energy) is about 4 to 10 times as effective as the same amount of energy absorbed from the secondary electrons produced by gamma rays. That is, the RBE for neutron/gamma is 4 to 10 for these experiments (Zirkle, *et al.*, 1946; Henschaw, *et al.*, 1946; Gray, *et al.*, 1940).

One rem is the estimated amount of energy absorbed in tissue which is biologically equivalent in man to 1 r of gamma- or X-rays. By definition:

$$1 \text{ rem} = \frac{83}{\text{RBE}} \text{ erg/gm tissue.}$$

In the absence of adequate human data, the tentative assumption of no species difference between man and other mammals is commonly made, and the RBE for fast neutrons to gamma rays is taken as about 5 for general effects on mammals. Then, for radiation protection in the case of fast neutrons:

$$1 \text{ rem} = \frac{83}{5} \text{ erg/gm tissue}$$

$$= 0.2 \text{ rep} = 0.1 \text{ n}$$

Roentgen-per-hour-at-one-meter, (rhm). The r per hr at 1 meter (rhm) is a physical unit of radioactive source strength. It is an unambiguous means of assigning a numerical value to the total "amount" of any radioactive substance which emits gamma rays or

X-rays, whether or not the disintegration scheme is known. The rhm is not a medical, radiological, dosage or protection unit. Thus 1 rhm of Co^{60}, for example, is that amount of Co^{60} whose unshielded gamma-ray emission produces 1 r per hr of ionization in air at a distance of 1 meter from the source. If this source were then enveloped in a spherical lead shield such that the transmitted gamma radiation produced only 0.1 r per hr at 1 meter, then the effective radioactive source strength of the shielded material would be 0.1 rhm.

The necessity of assigning a numerical value indicating the degree of radioactivity present in some sample is an everyday occurrence in many laboratories. For local use, it is often sufficient to cite the response of some stable readily available counter or electroscope. The non-uniformity of detection instruments in various laboratories makes such arbitrary readings of little use for intercomparisons between two or more laboratories. The situation is better if there are available in both laboratories beta- and gamma-ray counters whose absolute sensitivity as a function of "geometry" and of electron or photon energy is known. But even so, it is necessary to know the disintegration scheme of the radioactive isotope if the observations are to be reduced to absolute units. The use of curie or of rutherford units presupposes knowledge of the absolute number of disintegrating atoms per sec, and this can only be determined if the disintegration scheme is known.

TABLE 1

Gamma-ray Spectrum of Radium and Its Equilibrium Decay Products

Transition	*Average quanta per alpha ray of Ra* n	*Energy per photon (Mev)* $h\nu$	*Total photon energy (Mev)* $n \cdot h\nu$	*Compton absorption coefficient* σ_a *in* 10^{-5} cm^{-1} *std. air*	$n \cdot h\nu \cdot \sigma_a$ 10^{-5} $\frac{Mev}{cm\ air}$
Ra → Rn	0.012	0.184	0.0022	3.35	0.007
RaB → RaC	0.115	0.241	0.0277	3.56	0.098
	0.258	0.294	0.0758	3.68	0.279
	0.450	0.350	0.1575	3.77	0.594
RaC → RaC′	0.658	0.607	0.4000	3.81	1.523
	0.065	0.766	0.0498	3.74	0.186
	0.067	0.933	0.0625	3.66	0.228
	0.206	1.120	0.2310	3.51	0.810
	0.063	1.238	0.0780	3.44	0.268
	0.064	1.379	0.0882	3.37	0.297
	0.258	1.761	0.4540	3.13	1.42
	0.074	2.198	0.1626	2.93	0.476
Total	2.290		1.7893 *Mev*		6.19

Then:

$$1\text{ gm Ra} = \left(\frac{3.7 \times 10^{10} \times 3600}{4\pi \times 100 \times 100\,\text{cm}^2\,\text{hr}}\right)\left(\frac{6.19 \times 10^{-5}\ \text{Mev/cm}}{6.77 \times 10^{4}\ \text{Mev/cm}^3 \cdot \text{r}}\right) = 0.969\ \text{rhm}$$

Note that this numerical result is proportional to the value assumed for the absolute disintegration rate of radium. If the true value is found later to be less than 3.7×10^{10} disintegrations per second per gram radium, the expected value of rhm per gm of radium will be reduced in proportion.

At the beginning of 1947 the disintegration schemes of only about two dozen isotopes were known with certainty. This is only about 5% of the total of known radioactive isotopes.

Premature attempts to express activities in curie units have already led to unnecessary confusion. For example, the 6.5-day Mn^{52}, whose disintegration scheme has been established recently (Peacock and Deutsch, 1946) gives 3 photons (0.73, 0.94, and 1.46 Mev) for each disintegrating atom, but a beta ray is emitted in only 35% of the disintegrations. In the majority (65%) of the disintegrations, orbital electron-capture is the primary mode of radioactive decay, and is of course accompanied by X-ray and Auger electron emission. Thus even an absolute count of the rate of emission of beta rays from a Mn^{52} sample cannot be expressed as an absolute rate of disintegration without knowing this disintegration scheme. The number of beta rays is about ⅓ the number of disintegrations. Similarly the number of photons emitted is 3 times the number of disintegrations. Examples presenting other difficulties are numerous, *e.g.*, the 43-day Be^{7} and 65-day Sr^{85} are examples of isotopes which decay by electron-capture only, and give gamma rays and X-rays, possibly a few conversion electrons, but no beta or alpha rays at all.

Reasonably reliable interlaboratory comparisons of all isotopes which emit gamma rays can be made without knowledge of the disintegration scheme by using a standard instrument, technique, and unit. The roentgen unit, and instruments developed for its measurement, meets these requirements, and also has the advantage of not depending on the photon energy of the gamma rays.

Thus the source strength of any gamma-ray emitter can be expressed in terms of the number of roentgens per unit time produced at some arbitrary distance. Portable and reasonably inexpensive instruments reading in r per hr or mr per hr have been developed and are generally available as a result of recent advances in radiobiology and health physics. These usually have ionization chambers whose minimum linear dimensions are of the order of 10 cm; hence a convenient source-to-detector distance (center-of-source to center-of-chamber) is 1 meter. Accordingly, the roentgen-per-hour-at-one-meter (abbreviated "rhm") has been introduced recently as an arbitrary but unambiguous expression of the strength of any radioactive source which emits gamma rays.

TABLE 2

Some experimental values for rhm per gm of radium, in equilibrium with its short-lived decay products. The theoretical value, calculated from the data of Table 1, is 0.969 rhm, without any filtering. This is in satisfactory agreement with direct measurements of the effect of platinum absorption (Wilson, 1945, p. 35) which give about 0.94 rhm for zero platinum.

Author	*Filtration, mm* Pt	*rhm/gm* Ra
Taylor and Singer (1940)	0.5	0.816
Gray (1937b)	0.5	0.84
Mayneord and Roberts (1937)	0.25	0.88
	0.5	0.83
	2.5	0.63
	5.0	0.46
White, Marinelli and Failla (1940)	0.5	0.847

A number of careful experimental studies have been made of the gamma radiation from radium and its short-lived decay products. The number-energy distribution of these photons is complex. The disintegration of radium itself gives rise to a 0.184 Mev photon in 1.2% of the disintegrations. There are three principal lines following the beta-ray transition RaB → RaC, and eight important lines following the RaC → RaC′ beta-ray transition. The photon spectrum is shown in Table 1, and in Fig. 2.

Several of the more recent direct measurements of the gamma-ray source

TABLE 3

Milliroentgens per hour produced at one meter (mrhm) by the nuclear gamma rays and the annihilation radiation from the isotopes whose disintegration schemes are shown in Fig. 1. Small effects such as the bremstrahlung from inelastic collisions of beta rays with nuclei are neglected, as are also the soft characteristic X-rays emitted following orbital electron capture transitions, the small deficit of gamma rays in some transitions where internal conversion has been measured (*e.g., ca.* 0.5% in I^{130}), and the absorption of the gamma rays and annihilation radiation in 1 meter of standard air ($\sim 0.3\%$). The accuracy of the values for mrhm is the same as our knowledge of the nuclear gamma-ray energies, which is about ± 1 to 3%. Values of mrhm are given both for 10^8 disintegrations per sec (100 rd), and for 3.7×10^7 disintegrations per sec (37 rd) which in the case of RaB + C is 1 mc, or 1 mg Ra in radioactive equilibrium with its short-lived decay products. Isotopes such as H^3, C^{14}, P^{32}, S^{35} emit no γ radiation, hence have zero mrhm values.

Isotope	*mrhm/100 rd*	*mrhm/37 rd*
Na^{22}	3.52	1.30
Na^{24}	5.20	1.92
Mn^{52}	5.23	1.93
Mn^{54}	1.31	0.485
Fe^{59}	1.76	0.651
Co^{58}	1.51	0.560
Co^{60}	3.52	1.30
Zn^{65}	0.80	0.30
Br^{82}	4.06	1.50
I^{128}	0.049	0.018
I^{130}	3.39	1.25
I^{131}	0.59 to 0.71*	0.22 to 0.26*
RaB + C	2.27†	0.84†

* The degree of internal conversion of the 80-kev level in I^{131} is unknown. The lower limiting value of mrhm corresponds to complete internal conversion (i.e., no 80-kev gamma rays); the upper limiting value corresponds to zero internal conversion (i.e., one 80-kev gamma ray per beta disintegration). A 0.65-Mev gamma ray transition following about 10 to 15% of the beta rays of I^{131} has just been observed by C. L. Meaker, and tentatively confirmed by M. Deutsch. If, after further work, these numerical values are found to be substantially correct, then the mrhm values for I^{131} should be increased by about 6%.

† With 0.5-mm platinum filtration.

strength of 1 gm Ra and its short-lived products, in terms of rhm, are shown in Table 2. In general, these measurements are made on radium contained in a small capsule or "needle" having 0.5-mm platinum walls. The Pt walls absorb the alpha and beta rays completely, but they also attenuate the gamma radiation by approximately $10 \pm 2\%$ (Wilson, 1945, p. 34). The 0.5-mm Pt filtration is standard radiological practice in the therapeutic use of radium, hence is usually not corrected for in the determination of the rhm output. For radium, then, in equilibrium with its short-lived products, and with 0.5-mm Pt filtration:

1 gm Ra = 0.84 ± 0.02 rhm.

The Co^{60} isotope emits one 1.10 and one 1.30 Mev photon per disintegration, which have Compton absorption coefficients (excluding scattering σ_s) of $\sigma_a = 3.53 \times 10^{-5}$ and 3.41×10^{-5} per cm of air at 0° C and 760 mm Hg. Photoelectric and pair-production absorption are negligible for these energies in air. We can therefore anticipate that 1 rd (10^6 disintegrations per sec) of Co^{60} will produce at 1 meter (neglecting the absorption of about 0.3% in 100 cm of air path):

$$1 \text{ rd } Co^{60} = \frac{10^6 \times 3{,}600}{4\pi \times 10{,}000} \cdot \frac{(1.10 \times 3.53 \times 10^{-5} + 1.30 \times 3.41 \times 10^{-5})}{6.77 \times 10^4 \text{ Mev/cm}^3 \cdot \text{r}}$$

$$= 0.352 \times 10^{-4} \text{ rhm, or } 0.0352 \text{ mrhm}$$

while 3.7×10^{10} disintegrating atoms per sec would produce $3.7 \times 10^4 \times 0.352 \times 10^{-4} = 1.30$ rhm.

Similar calculations for a number of other isotopes which emit gamma rays are summarized in Table 3.

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Atomic Species Redefined

DR. TRUMAN P. KOHMAN of the University of Chicago's Institute for Nuclear Studies has recently proposed the word *nuclide* to express the concept of a particular species of atom, differing from all others in the constitution of its nucleus. This is derived from the prefix "nucle" (pertaining to the nucleus) and the Greek εἶδος (species, sort, kind), with contraction in the interest of euphony.

In recent years, the word *isotope* has come into use for this purpose, less by design than by default. *Nucleus* is likewise inadequate, since nuclei are rarely considered alone, but generally as constituents of atoms.

Definitions of these and related words are as follows:

Nuclide. A species of atom characterized by the constitution of its nucleus, in particular by the numbers of protons and neutrons in its nucleus.

Isotope. One of several nuclides having the same number of protons in their nuclei and, hence, belonging to the same element and occupying the same place in the periodic system.

Isotone. One of several nuclides having the same number of neutrons in their nuclei.

Isobar. One of several nuclides having the same number of nucleons in their nuclei and, hence, having (very closely) the same nuclidic weight.

Isodiaphere. One of several nuclides having the same difference between the numbers of neutrons and protons in their nuclei.

Isomer. One of several nuclides having the same number of protons and neutrons in their nuclei but existing in different levels of nuclear excitation.

. . . *American Journal of Physics* (July–August, 1947)

MANHATTAN DISTRICT DOCUMENTS

THIS IS A SUPPLEMENT to the list of Manhattan District Documents* begun with the tabulation of 267 declassified papers in the September NUCLEONICS. The editors will continue to make available in this form additional listings of the papers as they are made public.

Listed with the name of the paper are its author(s), MDDC (Manhattan District Declassification Code) number, and date of declassification.

The Future of Atomic Energy. E. Fermi. MDDC 1 (4/46)

The Spatial Distribution of Neutrons Slowed Down by Elastic Collisions. G. Placzek. MDDC 2 (4/46)

The Slow Neutron Cross Sections of Indium, Gold, Silver, Antimony, Lithium and Mercury as Measured with a Neutron Beam Spectrometer. W. W. Havens, Jr., L. J. Rainwater. MDDC 3 (4/46)

Neutron Beam Spectrometer Studies of Boron, Cadmium, and the Energy Distribution from Paraffin. L. J. Rainwater, W. W. Havens, Jr. MDDC 4 (4/46)

Energy of Neutrons from MsTh-D, La-D, Y-Be, and Sb-Be Photo Neutron Sources. A. O. Hanson. MDDC 149 (2/25/47)

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Radiocolloidal Behavior of Neptunium and Plutonium. Absorption of Plutonium (IV) at Trace Concentrations onto Glass. E. L. King. MDDC 393

The Fission Cross Section of Np 237. E. D. Klema. MDDC 394 (10/24/46)

New Models of Integrating Gamma-Ray and Slow Neutron Pocket Meters (Dosimeters) and Pocket Chambers. O. G. Landsverk. MDDC 395 (10/28/46)

A Survey Meter for the Measurement of Alpha, Beta, and Gamma Rays, Fast and Slow Neutrons. O. G. Landsverk. MDDC 396 (10/28/46)

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Isotope Techniques in Biochemistry — II

This paper, the second of a series, discusses isotopes for the study of reaction-mechanism and analytical problems. The techniques constitute a fairly precise, widely applicable tool of unusual reliability, used increasingly in biochemical fields

By NORMAN S. RADIN

National Institute of Health Junior Research Fellow
Biochemistry Department, Columbia University

Isotopes have been used in a fairly large number of studies of reaction mechanisms, but relatively little has so far been done with reactions of biochemical significance. An excellent piece of work, which illustrates a general technique, has recently been published by Doudoroff, Barker, and Hassid (*1*). A bacterial enzyme, previously called sucrose phosphorylase, was investigated. This enzyme had been shown to catalyze the reversible reaction:

glucose-1-PO_4 + fructose
= sucrose + phosphate.

When glucose-1-phosphate was incubated with inorganic radioactive phosphate in the presence of the enzyme preparation, but *without* the fructose, considerable activity was found in the organic phosphate, while dilution had occurred in the inorganic phosphate. The interpretation made, therefore, was that an intermediate enzyme-glucose compound is formed that is in equilibrium with inorganic phosphate:

glucose-1-PO_4 + enzyme
= glucose-enzyme + phosphate.

It is the glucose-enzyme complex that reacts with fructose (as well as several other sugars). Presumably, then, the following equilibrium also exists:

glucose-enzyme + fructose
= sucrose + enzyme.

This interpretation is confirmed by the ability of the enzyme to convert one disaccharide into another, apparently without the need for phosphate, as for example:

glucose-1-fructoside + sorbose
= glucose-1-sorboside + fructose.

The authors thus suggest the more appropriate name of "transglucosidase" for the enzyme.

A similar investigation, giving similar conclusions, has been made with succinic dehydrogenase (*2*). In this case the organic substrate was labeled, using deuterium.

Technique of Purification

An important technique peculiar to isotope work was used in the former work in the purification of the isolated glucose-1-phosphate. Called the "washing-out" method of purification, it permits very effective removal of contaminating isotopic material. After incubation of the glucose-1-PO_4 with enzyme and potassium phosphate, the enzyme was inactivated by boiling and the inorganic phosphate removed by a barium precipitation. A single precipitation, however, could not be expected to remove the inorganic phosphate quantitatively, and some radioactivity would show up in the remaining organic material. To wash out the remaining inorganic material, unlabeled phosphate was added and then reprecipitated with barium; repetition of this procedure brought the contaminating radioactive phosphate content down to a negligible amount. This method of purifying samples for isotopic analysis is a very general and useful one, and has been used for the stable as well as radioactive isotopes. When a sample is being recrystallized, the suspected contaminant (unlabeled) is added to the crystallizing solvent. When a cell suspension is being washed, unlabeled

contaminant is added to the wash water. This purification technique is most suitable for "yes-or-no" problems, where the exact isotope concentration is not needed and the only information desired is whether *any* isotope is present above the normal amount. It should be pointed out that, in the case of the stable elements, impurities that do not contain the element being analyzed are relatively harmless. Thus glutamic acid containing a trace of ammonia will give a misleading N^{15} content, whereas glutamic acid contaminated with salt is quite satisfactory. Incidentally, contamination by potassium should be kept low when working at low radioactivity levels, as natural potassium contains some activity due to the presence of K^{40}.

The reversibility of enzymatic reactions can be tested with the aid of isotopes. When a reaction goes very far in one direction, the amount of substance that might be formed by a reversal of the reaction may well be too small to pick up by ordinary isolation or analytical means. One can, however, start the usual reaction in the presence of a labeled decomposition product, stop the reaction before completion, and isolate the remaining *starting* material. The presence of isotope in the starting substance means that some synthesis has occurred and the reaction is therefore reversible. An example of this technique is the reaction studied by Smythe and Holliday (*3*), the degradation of cysteine by desulfurase to pyruvic acid, ammonia, and hydrogen sulfide. The degradation was begun in the presence of H_2S^{35} and stopped after about one quarter of the cysteine had been decomposed. The remaining amino acid was isolated and shown to contain radioactivity, indicating that the enzyme had catalyzed the reaction in both directions. In this, as in most enzyme work, it was necessary to demonstrate that exchange did not go on in the absence of the enzyme. In testing the reversibility of enzymatic reactions, even in non-isotopic work, one should try to exclude impurities, such as another enzyme, that might catalyze the reverse reaction through a different mechanism.

A similar test of reversibility was made by Chargaff (*4*) in a study of the action of pig kidney phosphatase on beta-glycerophosphoric acid. The enzyme preparation was allowed to hydrolyze the glycerophosphate in an alkaline medium containing radioactive phosphate. Recovery of the remaining ester gave a product free from activity, indicating that the reaction was irreversible.

Several interesting papers have been published (*5*) describing the use of deuterium for the study of the nature of the bacterial activation of hydrogen. The rates of equilibration of deuterium atoms between the gas and medium water were measured under various conditions.

Isotope Dilution Analysis

Introduced in 1934 by Hevesy and Hofer (*6*) and revived in 1940 by Rittenberg and Foster (*7*), isotope dilution analysis opens up immense possibilities in almost every field of chemistry. Basically, this technique consists of (a) the addition to an unknown mixture of some isotopically labeled compound, (b) the subsequent isolation of the same compound, and (c) determination of its isotope content. Since the unlabeled molecules of the compound of interest are identical with those of the added labeled compound, as far as the mixing and isolation procedures are concerned, the pure substance that is isolated will contain both species of molecules. The ratio of the two species clearly depends on the relative amounts of substance added and substance already present.

An important property of this method of analysis is that quantitative isolation is not necessary; all that is needed is a pure sample large enough for isotopic analysis. Since it is advisable to run several samples through the isotope analysis procedure to improve the precision of the result, one must isolate in most cases 4 to 100 mg of material, depending on the element and its concentration in the compound. The use of radioactive isotopes permits the

analysis of smaller samples, but it is necessary to know the actual size of the sample and this is frequently impossible to determine accurately in low ranges. Another limiting factor is that many of the usual criteria of purity cannot be applied at sub-milligram levels with present techniques.

Calculations

The nature of the calculations involved in isotope dilution work is quite simple. In the case of radioelements, there is the fundamental proposition that the specific activity is proportional to the concentration of the radioactive isotope. If the activity of W' grams of the labeled substance is A', the specific activity SA' is A'/W'. When this amount of material is added to an unknown mixture containing W grams of the same substance, the specific activity SA of the resultant mixture becomes $A'/(W' + W)$. Any pure sample subsequently isolated will have the same specific activity. From the two equations,

$$SA' = \frac{A'}{W'} \quad \text{and} \quad SA = \frac{A'}{W' + W},$$

one can calculate the desired value, W:

$$W = W'\left(\frac{SA'}{SA} - 1\right). \qquad (1)$$

A similar calculation is used for the stable elements, except that the atom % of the rarer isotope is used instead of the specific activity. An extra complication is occasionally introduced by the use of high isotope concentrations, so that the molecular weight of the labeled substance is appreciably affected. While the radioisotopes are used in atomic concentrations well below 1%, the stable isotopes of hydrogen and nitrogen are not infrequently used in concentrations of 99 and 32 atom % (respectively). A sample of glycine containing 32 atom % N^{15} would have a molecular weight higher than normal by about 0.3 units.

Suppose W' grams of labeled substance of molecular weight M', containing n atoms per molecule of the labeled element are to be added to an unknown mixture. If the labeled element contains A' atom % of the rarer isotope, the total number of gram-atoms of the rarer isotope present is equal to $n(W'/M')\ (A'/100)$. The unlabeled substance present in the unknown mixture has the normal values of M and A, and the same value of n. The number of gram-atoms of the rare isotope in the unknown is then $n(W/M)(A/100)$. The total number of gram-atoms of the isotope present after mixing is equal to the sum of these two terms:

$$N_r = n\left(\frac{W'A'}{100\,M'} + \frac{WA}{100\,M}\right).$$

A similar consideration shows that the total number of gram-atoms of the *common* isotope in the mixture is

$$N_c = n\left(\frac{W'[100 - A']}{100M'} + \frac{W[100 - A]}{100M}\right)$$

(When more than two isotopes of the element are present, the term "common" includes all isotopes other than the one employed for labeling). The concentration, in atom %, of the rarer isotope in the final mixture is, by definition,

$$A_{\text{final}} = \frac{100N_r}{N_c + N_r}.$$

Any sample that is subsequently isolated will have the same value. Substituting for N_c and N_r gives:

$$A_{\text{final}} = \frac{W'A'M + WAM'}{W'M + WM'}.$$

It is a little more convenient to use the atom % *excess* values, which are obtained by subtracting the normal abundance from the observed abundance. If X_0 is the atom % excess in the original labeled material, and X the same for the isolated material, we have $X_0 = A' - A$ and $X = A_{\text{final}} - A$. Substitution in the previous equation gives the working equation:

$$W = W'\left(\frac{X_0}{X} - 1\right)\frac{M}{M'}. \qquad (2)$$

This equation is very similar in form to that derived for radioactive labels,

except that provision is made for a correction due to the molecular weight effect. It should be noted that n does not appear in the final equation.

The magnitude of the error caused by neglecting the molecular weight term must be estimated for each experiment. In the 32 atom % N^{15} glycine mentioned earlier, $M/M' = 0.996$. Omitting this term would introduce an error of 0.4% in W, which is barely within the range of significance. Use of such high isotope concentrations in analytical work is rarely necessary.

Precision Considerations

In general, when $y = f(x_1, x_2, x_3, \ldots)$, the percentage error in y that results from a percentage error (Δx_1) in x_1 is equal to

$$\left(\frac{\partial y}{\partial x_1}\right)_{x_2, x_3, \cdots} \frac{x_1}{y} \Delta x_1$$

This expression can be used to calculate the errors introduced by errors in W', X_0, and X. The percentage error in W due to X_0 is

$$\left(\frac{\partial W}{\partial X_0}\right) \frac{X_0}{W} \Delta X_0 = \frac{W'}{X} \frac{X_0}{W} \Delta X_0.$$

Substituting from equation 2 converts this to $\left(\frac{W'}{W} + 1\right) \Delta X_0$. Examination of this term shows us that the precision of W depends not only on the precision with which X_0 is determined, but also on the ratio of the values of W and W'. Assuming a value of 1% for ΔX_0, the following table can be set up:

Percentage error in W	$\frac{W'}{W}$
infinity	infinity
10	9
3	2
1.5	0.5
1.1	0.1
1.01	0.01

It can be seen from the table that the addition of a smaller amount of labeled material results in diminution of the error resulting from errors in isotopic analysis. The diminution is clearly asymptotic, and a W'/W ratio less than 0.2 or so yields little improvement in precision. (The M/M' term has been omitted in these calculations because it is so close to one.) By estimating from previous analyses, it is usually possible to choose a value of W' that will lead to a favorable ratio. When very small samples are being analyzed, it is sometimes necessary to add more labeled material than is desirable because the yield of isolated material might otherwise be too small. The relationship just derived holds for X, SA, and SA' as well as for X_0.

Examination of equations 1 and 2 shows that an error in W' of 1% produces an error of 1% in the final answer. Normally, the labeled material that is added can be weighed out with very high precision, so that a negligible effect on the final precision is obtained from this source. The recent developments in microcounter-current methods of isolation may soon permit work with very small unknown samples, however, and in such cases the weight of labeled material cannot be determined so accurately.

The over-all precision of the isotope dilution method is equal to the square root of the sum of the squares of the individual errors. Since modern mass spectrographs can supply most values with an uncertainty of about 0.3%, the dilution technique will give an answer with an uncertainty of about 0.5%. In the case of radioactive tags, the over-all precision is about 2% with modern instruments. It is assumed that a favorable W'/W ratio is used.

Purity Considerations

Usually, the greatest source of uncertainty in the isotope dilution method is the question of purity. The added labeled compound can normally be prepared in very high purity, so that little doubt enters here. The isolation of equally pure material from a mixture is frequently quite difficult. No error at all is produced by contamination with material that does not contain the labeled element. Thus, the presence of water in a sample of isolated leucine labeled with heavy nitrogen will not

TRACER MICROGRAPHY USED TO DETECT RADIOISOTOPES

A METHOD FOR THE TRACING of radioactive isotopes in materials in which they have been intentionally introduced has been developed by L. Marton of the National Bureau of Standards with the cooperation of P. H. Abelson of the Dept. of Terrestrial Magnetism, Carnegie Institution of Washington. By means of a magnetic focusing arrangement, the radiation given off by a radioisotope within a sample material is made to form an image of the emitting surface upon a photographic plate. The image may then be used in studying the distribution and concentration of the radioactive element present in the sample.

This method improves on the resolution that could be obtained with the well-known radioautography process. The former uses electron optical image formation for determination of the distribution of a radioactive element within a sample. Called "tracer micrography," it is based on the emission of high-speed electrons (beta rays) by many tracer elements and the use of magnetic lens elements for forming an image on a suitable recording surface.

Gallium chloride, which emits electrons of uniform speed and is prepared by chemical separation from zinc, was bombarded by heavy hydrogen nuclei in the cyclotron at the Carnegie Institution, and the solution was evaporated drop after drop on a ¼-in. tantalum disk. Radiation emitted from the surface of the disk, upon passing through a magnetic lens consisting of a small iron-clad coil with Armco iron pole pieces, was brought to a focus on a photographic film at a distance of about 3½ in. An image of the disk was thus obtained, showing radioactive areas.

For calibration of the instrument, the photographic film was replaced by a Geiger counter, and the lens current necessary to produce a maximum number of counts in unit time was determined for radiations of varying velocities. This set the focusing current for a given radiation.

Micrographs with good definition were obtained consistently when the radioactive layer was sufficiently thin to avoid considerable self-absorption. The best resolving power attained so far has been 30 microns.

affect the N^{15}/N^{14} ratio. The presence of 1% isoleucine in the leucine, however, will lower the value of X by 1% and will therefore give an answer that is 1.1% too high (assuming a W'/W ratio of 10). If a radioactive compound is used as such for the activity determination, the presence of *any* type of impurity will result in an error, unless an elementary analysis is also done and the specific activity recorded in terms of the element, and not the compound.

The biochemist is frequently interested in the determination of optically active substances. The preparation of optically active isotopic compounds, however, is usually somewhat more tedious or difficult than the synthesis of racemic mixtures, and it is fortunate that the use of the latter for dilution analysis is permissible. It is necessary then to take special pains to isolate only the proper optical form, since even a small amount of the other isomer will greatly affect the isotope concentration. Consider a dilution analysis with a radioactive tag: Let us add 20 mg of a racemic mixture with an activity of 1000 counts per min per mg (cpm/mg) to a mixture containing 100 mg of the optically active substance. According to equation 1, the specific

radioactivity of the isolated optically active substance should be $\frac{1}{11}$ of the original. If 50 mg are actually isolated, the activity observed should be $50 \times 1000/11$, or 4545 cpm. If only $\frac{1}{2}$ mg of the *other*, highly radioactive optical isomer is present, there will be observed an extra 0.5×1000, or 500 cpm. (The natural isomer, with only 49.5 mg present in the sample, will then supply only 4500 cpm.) The observed figure of 500 + 4500, or 5000 cpm, on conversion to specific activity and substitution into equation 1, indicates that 90 mg of the natural substance had been present originally. This represents an error of 10%, arising from an error of only 1% in purity. It should be noted that the errors due to impurities depend in part on the ratio of W'/W.

Outside of the usual methods of checking the purity of an isolated sample, there is available to the investigator the technique of examining the isotope concentrations of mother liquors and successively recrystallized samples. Purity is indicated by constancy of the analytical values, as well as by agreement between isotope concentrations in mother liquors and crystals. When several dilution analyses for various substances are made on the same mixture, as may happen when little material is available, it is advisable to use the same element in the same isotopic concentration for labeling each substance. In this way, impurities tend to have the same isotope concentration as the isolated substance, thereby diminishing the error.

It has been found not infrequently that the ordinary methods of purification have definite limitations. Even though successive recrystallizations may give the same analytical data, a small amount of impurity may persist, perhaps occluded or adsorbed on the crystals. Moreover, the differences in the elementary analyses of the members of a group of compounds (amino acids, fatty acids, etc.) are often close to the normal analytical uncertainty. When a contaminant is suspected, one should, if possible, check the suspicion by means of a specific color test. Persisting contaminants can often be removed by purification through formation of a derivative. Of special value in isotope work is the "washing-out" technique, which has been discussed fully in the section on reaction-mechanism studies. The recent developments in the field of counter-current separations are of great interest in this connection. In general, when a labeled racemic mixture is used, the amount added should be kept as low as possible to minimize the danger of contamination with the wrong optical form.

Inverse Isotope Dilution

In many cases it is possible to start with a mixture that contains as the unknown a substance that is *already* isotopically labeled. The analyst can then add a known amount of *un*labeled compound, isolate the substance, and determine its isotope concentration. This technique, which might well be called "inverse isotope dilution," is very similar in principle to the usual type of isotope dilution analysis and similar considerations apply. Two distinct advantages can be obtained by this inversion: (a) Very small amounts or concentrations can be determined, and (b) the pure diluting compound that is added need not be made labeled.

As was pointed out in the section on precision, the usual dilution technique requires the analyst to add less than one fifth of the amount of substance present if good precision is to be obtained. Thus, if a 5-gm sample of protein, containing 2% arginine, is to be analyzed, the investigator cannot safely add more than 20 mg of isotopic arginine before isolating. This places a lower limit on the amount of mixture that can be used, the actual value depending on the efficiency of the isolation method, the concentration of the compound of interest, and the isotope-analysis procedure.

When inverse dilution is used, equation 1 can still be used, but the meaning of the symbols must be changed slightly. Let W' refer to the weight of substance originally present, SA' to its specific

activity, W to the weight of normal material added, and SA to the specific activity of the sample isolated. For convenience, W', instead of W, is solved for:

$$W' = W\left(\frac{SA}{SA' - SA}\right). \qquad (3)$$

With the usual precision criteria, the percentage error in W' due to a percentage error (ΔSA) in SA is:

$$\left(\frac{\partial W'}{\partial SA}\right)\frac{SA}{W'}\Delta SA = \left(1 + \frac{W'}{W}\right)\Delta SA. \qquad (4)$$

From this equation it is seen that the more unlabeled material added, the lower the uncertainty in the answer. This happy situation thus enables one to work with very low values of W' and, in general, eases the problem of isolation. In practice, the original isotope concentration sets a limit on the amount of unlabeled material that can be added. If, for example, the original specific activity is 20,000 counts per minute per gram (cpm/gm), and it is desired to obtain a sample with a specific activity of 400 cpm/gm, the amount of diluting material that should be added is W' (2000 − 400)/400 or 49W'. In other words, a 50-fold dilution is permissible. Similar considerations apply to work with the stable isotopes; here, the extent of dilution permissible tends to be less.

Purity a Limiting Factor

When the original mixture contains more than one substance labeled with the same isotope (or radioelements with similar radiation characteristics), purity becomes an important limiting factor. In the above example, the original material constitutes only 2% of the total sample being analyzed. If another substance with a similar specific activity is contaminating the isolated sample, the presence of 2% will double the observed activity and thereby give rise to an error of about 100%. The presence of only 0.1% impurity will result in a value 5% too high. Since it is usually quite difficult or impossible to isolate samples with a purity greater than 99.9%, it becomes evident that the presence of potential isotopic contaminants requires the use of smaller dilution factors. The "washing-out" technique is highly advisable in such cases.

If, on the other hand, only *one* substance in the mixture is labeled, impurities can have only little effect on the observed specific activity or atom % excess value. From equation 4 it can be seen that 1% impurity produces a 1% error in W' (assuming a small value for W'/W). If the impurity lacks the element being used as a label, the error can be eliminated. The addition of large amounts of unlabeled material not only decreases the importance of an impurity, but also tends to decrease the likelihood of an impurity appearing in the isolated material.

Second Advantage of Inverse Method

The second advantage of the inverse dilution method is that the diluting compound need not be made with an isotopic label. The inglorious task of developing a new synthetic approach that permits introduction of an isotope in good yield is thereby eliminated. The investigator can often use a purified commercial product or a synthetic product made by standard methods. Frequently it is easier to obtain a compound of biological interest by isolation than by synthesis. This is especially true when optically active substances are wanted. Indeed, there are compounds which at present cannot be synthesized at all; for these, the inversion of the usual isotope dilution technique is almost mandatory.

Labeled mixtures can be prepared in several ways. The simplest involves running a chemical reaction using a labeled reactant. The resultant mixture can be analyzed for suspected reaction products by adding unlabeled substances, isolating them, and determining their isotope contents. This method should prove useful in studies of enzyme and tissue-slice reactions.

Possibly the most interesting labeled mixture is the one prepared by feeding an isotopic substance to an organism. For example, the mold *Neurospora* has

been grown in this laboratory on a medium containing heavy ammonia as its sole source of nitrogen (except for a trace of biotin). This sample of *Neurospora* can now be analyzed for its content of any nitrogenous substance that can be isolated. Deuterium oxide in the mold's medium cannot be used in the same way, as some hydrogen is incorporated into the mold from the organic food supplied. It should be recalled that a knowledge of the isotope concentration of the undiluted substance in the mixture is necessary. Since there would be an indeterminate amount of dilution of the deuterium, varying for different substances, this label would be useless. However, it may be that sufficient equilibration of *Neurospora*-bound hydrogen and medium water hydrogen occurs, so that the deuterium concentration of *Neurospora* hydrogen can be obtained by analysis of the medium water at the end of the growth period.

Labeling of Higher Organisms

Higher organisms can also be labeled by feeding or injecting an isotopic compound, but additional complications appear. A single source of nitrogen, carbon, hydrogen or oxygen cannot be used for the more complex organisms since they have complex food requirements. Thus, the amino acids of a rat cannot be labeled with a known concentration of heavy nitrogen by feeding heavy ammonia because some of them must be supplied in the diet and interchange of nitrogen atoms would produce an indeterminate dilution. However, the remaining elements found in organisms can be used since they can be supplied from one source. For example, a rat could be fed a phosphorus-free diet supplemented with radioactive phosphate and then analyzed for its various phosphorous-containing constituents by adding the unlabeled substances to the homogenized rat (or its organs), isolating the substances and measuring their specific activities.

In order that the isotope concentration before dilution in the substance of interest be known, it is necessary to feed the isotopic material to the organism long enough for the latter to increase in weight many fold or long enough for the previously present unlabeled material to be replaced by new material. Organisms that can be grown from a few cells to the desired stage in an isotopic medium are admirable. Egg-laying animals can be grown readily over a period of considerable weight increase by injecting the isotopic material through the egg shell. In the case of full-grown animals, the time required for replacement of unlabeled body constituents by isotopic substances may run into weeks.

Essential Compounds

The element being used for labeling need not be supplied in one compound alone, however, if the substance of interest cannot be synthesized by the organism. Thus, an essential amino acid, labeled with isotopic carbon, could be fed together with a diet lacking that amino acid, until all of that acid already present in the animal has been replaced by the isotopic form. The individual organs or purified proteins could then be hydrolyzed, diluted with the unlabeled amino acid, and the acid then isolated and analyzed. Even though a compound *B* is synthesized by an organism, if it is derived from an essential (unsynthesized) compound *A*, the inverse dilution technique can be applied by feeding isotopic *A* (together with a diet lacking *A*) until all of the organism's *B* has been replaced by *B* of known isotope content. Sometimes, only *part* of a molecule is essential to an organism, and labeling this part permits analysis for conversion products. Thus, it might be possible to raise an animal on a diet freed of labile methyl groups except for methionine labeled with C^{13}, C^{14}, D, or T in the methyl group. In due time, the methyl groups of the animal's methionine, choline, creatine, creatinine, and lecithin will have a known isotope concentration. Addition of known amounts of these substances, unlabeled, to homogenates of the animal's organs and subsequent isolation and isotope analysis permit cal-

culation of the contents of these methylated body constituents. Since a small amount of synthesis of methyl groups seems to occur (*24*), it might be advisable to use deuterium as the label and add enough heavy water to the feed to equalize the isotope concentrations in the water and methionine methyl group. As more knowledge about metabolic reactions becomes available, this method of analysis may become more important.

Applications of Isotope Dilution Principles

Most isotope dilution work has been done with the amino acids of proteins, usually using racemic amino acids labeled with N^{15} for diluting. The general technique consists of hydrolyzing a known amount of pure protein with 20% HCl, addition of one or more labeled acids, and isolation of the L-acids or their derivatives. A general summary of the work in this field has been prepared by Shemin and Foster (*8*).

The method of isolation chosen should result in isolation of the L- rather than the DL-form. With glutamic acid, the usual method (crystallization as the hydrochloride) will permit isolation of the correct isomer; tyrosine must be purified through the copper salt. In choosing a derivative, preference should be given to the derivative with the higher molecular weight, because the yield usually will be higher and will permit additional purifications.

One of the difficulties encountered in protein analysis is the question: How much decomposition has occurred during the hydrolysis step? Since many other chemicals of natural occurrence are conjugated and must be hydrolyzed before pure material can be obtained, the question is equally valid for them too. The destruction of tryptophan during acid hydrolysis is well known; that of phenylalanine less so (*9*). Unfortunately, there appears to be no method at present to tell us whether the peptide and other protein linkages do not somehow labilize the bonds inside the amino acids.

The problem of the stability of the freed amino acids can be attacked simply by heating an amino acid with the hydrolytic medium, possibly adding other amino acids and protein-linked substances. The stability of serine has been studied by a dilution experiment (*10*). It was felt that serine might be converted in part to glycine, so serine and isotopic glycine were refluxed with hydrochloric acid and the glycine subsequently isolated. Since no dilution of the glycine N^{15} had occurred, it was concluded that no glycine had been formed from the serine. It might be interesting to repeat this experiment with the inclusion of other amino acids or sugars.

When racemization occurs during a process, or some racemic material is present in the unknown, the amounts of each isomer can be determined by the isotope dilution method by adding labeled racemic material and then isolating both the L- and DL-forms. A simple extra calculation is necessary. Let the isotope concentrations (or specific activities) of the various forms be designated as X_L, X_D, and X_{DL}. Then we have:

$$X_{DL} = \tfrac{1}{2}X_L + \tfrac{1}{2}X_D.$$

Since the values of X_{DL} and X_L are known from the isolated samples, it is possible to calculate X_D. Substitution of this value into the usual dilution equation gives the amount of D-isomer that was present. Incidentally, it should be remembered that the value of W' that must be used in the equations is actually only one half the weight of the racemic compound added. Using this technique, several workers (*23*) have investigated the glutamic acid of various tumors and found it to be free, within experimental error, of any D-glutamic acid. If the D-isomer predominates in the unknown mixture, the D- and DL-forms will normally be isolated, but the calculation is very similar.

Modification of Inverse Method

A modification of the inverse dilution method has been introduced recently for protein analysis (*11*). A small amount of protein hydrolysate is treated with "PIPSYL chloride" (p-iodophenylsulfonyl chloride) in a manner designed to ensure quantitative reaction with the

amino acids. The iodine is radioactive. To the mixture of sulfonamides is added a large amount of the unlabeled iodobenzenesulfonyl derivative of the amino acid of interest, and the compound subsequently isolated and its specific activity determined. This procedure has the advantages and disadvantages of the inverse dilution method, as discussed above. The need for high purity in the isolated compound is great, owing to the fact that all the potential impurities are also labeled. It seems likely that attaching such a large group might make some of the amino acids even more similar in their properties and therefore harder to separate.

Of incidental interest to the biochemist is the use of heavy oxygen and carbon for the elemental analysis of compounds (*12*). Those research groups possessing mass spectrometers may find these methods superior to the present ones, the direct analysis for oxygen being perhaps the more interesting.

In Vivo Isotope Dilution

The use of dilution analysis is not restricted to inanimate mixtures, but a few special considerations apply to analyses made with living organisms. There is first the question: How complete is the mixing in the organism? The complexities introduced by the phenomena of selective permeability, adsorption, diffusion and metabolic changes make this question difficult to answer with assurance. The completeness of mixing can be checked to a certain extent by analyzing the dead and homogenized organism, or by comparing the analytical results with those obtained by other methods. Assuming complete mixing does take place, the time necessary for this can be judged by performing analyses at successive intervals and plotting the values against time. As mixing occurs, the curve will climb or fall, then level off, and then fall as excretion occurs. The time required for equilibration is usually close to that indicated by the point of inflection.

In vivo analysis is restricted to substances that are not metabolized or are metabolized at a rate that is quite low compared to the time needed for equilibration. If the ingested or injected isotopic compound is excreted or converted to another substance before fairly complete mixing occurs, the calculated value will be in error.

Body Water Determination

The simplest *in vivo* analysis that can be done is the determination of the water content of an organism. In 1934, Hevesy and Hofer (*6*) measured the water content of a human by ingesting heavy water and analyzing the water of the urine. This problem has been investigated further by Moore (*13*) with deuterium oxide and by Pace *et al.* (*14*) with tritium oxide. Since the hydrogen of many biological compounds exchanges readily with the hydrogen of water, a small extra dilution, estimated at 5% (*13*), takes place. In the one hour required for complete mixing, negligible loss occurs in the urine and negligible hydrogen is added by oxidation of food. It has been pointed out (*14*) that analyses of this type suffer from a certain amount of variability due to variations in the amount of fat and other substances present in the different individuals in a species. The same is true, of course, for analyses made of organs and tissues. In the latter case, it might be advisable to perform some fractionation before analyzing. The isotopic method of determining water volume illustrates the advantages of this technique for clinical work.

A similar *in vivo* analysis has been made (*13*) of the potassium content of the human body. Radiopotassium was injected, allowed to equilibrate, and the specific activity of the red cells determined. Since over one day is required for the mixing, it is necessary to analyze the urine and subtract the total excreted activity from the activity injected. The use of red cells as a source of a sample of body potassium is notable, and suggests the possibility of similar uses. Red cells constitute a clean and fairly uniform tissue, portions

of which can be obtained often and readily from the same animal.

Attempts have been made to adapt isotope dilution to the determination of the extracellular water space, but complete success still remains to be obtained (*13, 15*). Radioactive sodium and chlorine have been used, but too rapid entrance into the intracellular space and other complications have resulted in figures that seem to be too high. There is still need for a substance that is restricted, possibly for one hour, to the extracellular fluids.

Use of Labeled Red Cells

A powerful tool for the study of blood changes, particularly in shock, has been the use of labeled red cells. The rate of synthesis of red cells is quite low (0.8% per day in humans), and the time required for mixing only a matter of minutes, so that very accurate analyses can be made. The erythrocytes can be labeled by incubating in radiophosphate solutions (*16*) and injecting a known volume of washed cells, or by injecting low levels of radiophosphate over a period of time and then injecting an aliquot of blood (of known hematocrit) into another animal (*17*). Although these means of labeling permit a slight exchange of isotope with the plasma, the extent is negligible in the short interval required for mixing.

Somewhat more work has been done with red cells labeled with radioactive iron (*18, 19*). Since hemoglobin iron does not exchange with iron ions, it is necessary to use cells synthesized by another animal that had been given the isotopic iron. In some experiments, two different aliquots of red cells labeled with different isotopes of iron, Fe^{55} and Fe^{59}, were injected into the same animal. The radiations of the two differ sufficiently to permit their individual analyses on the same blood sample. The usefulness of the two tags derives from the fact that one can determine the volume of circulating red cells in the same animal *twice* in the course of an experiment. The use of additional labels (P^{32}, N^{15}, etc.) would permit the analysis to be made more than twice in the same animal. In general, the use of several isotopes in the study of one substance in the same animal saves much work, since the animal is its own control.

Interesting studies of plasma volume have been made with plasma protein labeled with I^{131}, as well as other elements (*19, 20*). The proteins were labeled by shaking the radioiodine with defatted plasma, the iodine probably entering the protein tyrosine moieties on the benzene ring.

The presence of D-amino acid oxidase in the body has raised the question as to what its function is. One possibility is that the body normally synthesizes its amino acids symmetrically and then destroys the D-forms. To test this possibility, Shemin and Rittenberg (*21*) fed fairly large amounts of isotopic DL-glutamic acid to rats and isolated the overflow D-glutamic acid from the urine. (The L-isomer is almost completely utilized or destroyed). No dilution of the D-acid was found, indicating that the synthesis of glutamic acid is asymmetric. In an experiment with tyrosine, the greater sensitivity inherent in the inverse dilution method was utilized. Heavy ammonia and DL-tyrosine were fed over a period of time and the urinary D-tyrosine isolated and analyzed. If even a trace of D-tyrosine had been synthesized from the ammonia, it would have shown up by the presence of some heavy nitrogen in the isolated material.

Difficulty of Obtaining Samples

Similar *in vivo* dilution studies were made by Bernhard (*22*) with deuterium-labeled dicarboxylic acids. Previous work had indicated that a certain amount of fatty acid combustion goes through the path of omega-oxidation. The deutero 6, 8, and 10 carbon dicarboxylic acids were fed to dogs, isolated from their urine, and found to be undiluted. Apparently, then, these acids do not normally exist in the body.

The attractiveness of *in vivo* dilution experiments is limited by the difficulty of obtaining samples of the substance of interest. The blood, urine, and feces are the best sources of samples, but not

many substances can be obtained from them. A trick to remember is that some compounds can be made to appear in the urine by allowing them to conjugate. The so-called detoxification reactions are of great value here. Care should be taken to use minimum amounts of the foreign substances so as to prevent stimulation of the synthesis of the conjugating material. For example, one might feed a small amount of benzoic acid and carbon-labeled glycine and then isolate and analyze the urinary hippuric acid. If the glycine fed equilibrates rapidly enough with the body glycine, the glycine used for coupling will be diluted to an extent indicated by the usual dilution equation. Actually, the value obtained might well refer to the "pool" of free body glycine, rather than the total (including protein-bound) glycine. Of interest in this connection is the paper by Rittenberg and Schoenheimer (*9*). A danger in this method is that the chemical used by the body for the conjugation might not be the one it seems to be. If the precursor is not in equilibrium with the diluting compound, this will be indicated in the isolated material by either complete absence of the tagging isotope or by a low value.

Value of Isotope Dilution Analysis

Isotope dilution analysis is frequently tedious and complex and requires expensive equipment and highly skilled workers. Because of these factors, the routine use of dilution analysis will probably be restricted to relatively few applications. The high degree of certainty for most isotopic analyses, however, will make them popular for the confirmation of other analytical methods. For some analytical problems, there is no other tool available. Extension of the isotope techniques to many types of analyses should be expected in the next few years as more workers enter the isotope field.

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Applications of Probability Theory to Nuclear Particle Detection

By L. J. RAINWATER and C. S. WU
Pupin Physics Laboratory, Columbia University

THE RANDOM NATURE of the fundamental processes involved in the emission and detection of nuclear particles leads to many important differences between such measurements and most ordinary physical measurements. Since it has been the experience of the authors that a proper appreciation of these factors requires good understanding of the basic principles involved, emphasis has been placed on the derivation of all relations from elementary considerations.

The following problems will be considered: (a) If the "mean" expected value for a count is u, what is the probability $P_n(u)$ that exactly n counts will be obtained? (b) If n counts are actually obtained, what is the probability that the "mean" expected value lies between u and $(u + du)$? (c) If a counter, counter circuit, or mechanical register has a "dead" (insensitive) time τ after each pulse, what fraction of the (random) input pulses will not be detected due to this effect (counting losses)? (d) What is the theory of the regularizing action of a scale-of-m scaling circuit in reducing counting losses by a mechanical register?

Before these main problems are discussed, it will be useful first to consider a few elementary problems, the solutions of which will facilitate the derivation of the basic relations which will be needed later. For this purpose, the following simple problems, involving successive throws of a single die, and other problems will be used.

Introductory Problems

1. What is the probability that a given result will be obtained on a single throw of a die? **Soln.** Since all numbers from 1 to 6 are equally probable, the apriori probability is $p = \frac{1}{6}$.

2. What is the probability of *not* throwing a given number on one throw of a die? **Soln.** Since there is unit probability that *some* result will be obtained, the probability is 1 minus the probability, $\frac{1}{6}$, that the given number *will* be thrown. Thus, $p = 1 - \frac{1}{6} = \frac{5}{6}$.

3. What is the probability that the given sequence, [3, *4*, 2, *6*, 5], will be obtained on five successive throws? Here *4* and *6* mean that the 4 or the 6 should *not* be thrown on the given throw. **Soln.** In order that the complete sequence be obtained, it is necessary for each successive step to be satisfied. The five steps have the separate probabilities $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{6}$. The probability is $\frac{1}{6}$ that the first throw will be successful. *If* it is successful, then the chance is $\frac{5}{6}$ that the next step will be successful, etc. The total probability for the complete sequence is thus the *product* of the separate probabilities of the individual steps and $p = \frac{1}{6} \times \frac{5}{6} \times \frac{1}{6} \times \frac{5}{6} \times \frac{1}{6} = (\frac{1}{6})^3(\frac{5}{6})^2$.

4. What is the probability of throwing *exactly one* 6 in five throws? **Soln.** Any successful sequence of throws must have one throw giving a 6 and four throws *not* giving a 6. From problem 3, the probability p_1 of such a sequence is $p_1 = (\frac{1}{6})(\frac{5}{6})^4$. The *total* probability is the *sum* of the separate probabilities of all possible sequences that will lead to the correct result. Since all successful sequences have the same probability p_1, the total probability is just p_1 times the number of permitted sequences. Since, in this case, a given successful sequence can be expressed in terms of the number of the throw on

A thorough elementary development and discussion of the theory of statistical accuracy, counting losses, and scaling circuit regularizing action. This is the second of a series of articles devoted to the principles underlying the design and use of radiation measuring and detection instruments

which the 6 occurs, there will be just five possible places for the six to occur and $P = 5p_1 = 5(\frac{1}{6})(\frac{5}{6})^4$.

5. How many *different* groups of n different numbers can be chosen from the numbers 1 to N? Two "different" groups must have at least one of their numbers different. (The same n numbers arranged differently do *not* constitute a new group!) **Soln.** The first number selected may be any of the N numbers so there are N ways of choosing it. *After* the first number has been selected, there are $(N-1)$ numbers from which the second number may be chosen. After the first and second numbers have been chosen, there are $(N-2)$ numbers from which the third may be chosen. Thus, there are $N(N-1)(N-2)\cdots(N-n+1) = N!/(N-n)!$ ways in which n numbers may be selected from N numbers. This, however, includes not only all different groups of n numbers, but also all *arrangements* of the chosen numbers.

To obtain the number of different *groups*, we must divide the above result by a factor equal to the number of ways n numbers may be arranged. Thus (1,2,3), (1,3,2), (3,1,2), (2,1,3), (2,3,1) and (3,2,1) are the six possible arrangements for the three numbers indicated. With n numbers, there are n choices for first position, $(n-1)$ choices for second position *after* the first position is selected, etc. This gives the "arrangement factor" $= n!$ The required result is

$$\left[\frac{N!}{n!(N-n)!}\right] = \text{number of groups} \quad (1)$$

6. What is the probability of throwing exactly n sixes in N successive throws of a die? **Soln.** A given successful sequence requires n throws giving 6 and $(N-n)$ throws *not* giving 6 and, from problem 3, has the probability $p_1 = (\frac{1}{6})^n(\frac{5}{6})^{N-n}$. The number of possible successful sequences is the number of ways the n throws for 6 can be selected from the N total throws. From problem 5, this is just $N!/n!(N-n)!$ giving

$$P = \left(\frac{1}{6}\right)^n\left(\frac{5}{6}\right)^{N-n}\frac{N!}{n!(N-n)!} \quad (2)$$

The above examples have developed the necessary relations for the solution of the counting problem which will first be stated in a restricted fashion for simplicity and later in a more general fashion.

Restricted Statement of Problem

Assume that in a counting device for the detection of radioactive disintegrations there are exactly N radioactive atoms present in a sample at the start of the counting period and that each has the same probability p of disintegrating and producing a count during the counting interval. Then what is the probability P_n that exactly n counts will be obtained during the counting period? (Note that p is the *product* of the separate probabilities that a given atom will disintegrate, times the probability that the given disintegration will be detected in the given time interval. In general, either or both of these separate factors may be very small so that p is usually very small.)

Solution. This problem is exactly similar to problem 6 above. Here the tabulation of whether each atom will or will not give a count corresponds to whether each throw of the die will or will not give a 6. The term p replaces $(\frac{1}{6})$ and $(1-p)$ replaces $(\frac{5}{6})$ to give

$$P_n = p^n(1-p)^{N-n}N!/n!(N-n)! \quad (3)$$

This problem is known as *Bernoulli's problem* having equation 3 as the solution. It is of interest to consider some of the properties of the solution.

Since *some* result must be obtained

$$\sum_0^N P_n = [p + (1-p)]^N = 1 \quad (4)$$

The term P_n is the $(n+1)$th term in the above-indicated binominal expansion. The mean value $u = n_{av}$ is

$$u = n_{av} = \sum_0^N nP_n = \sum_1^N nP_n$$

$$= pN \sum_0^M \frac{p^m(1-p)^{M-m}}{(M-m)!m!} M! = pN$$

where $M = N - 1$ and $m = (n-1)$ and equation 4 is used.

Thus

$$u = n_{av} = Np \quad (5)$$

Similarly n_{av}^2 is of interest.

$$n_{av}^2 = \sum_0^N n^2P_n = \sum_1^N n^2P_n$$

$$= Np \sum_0^M (m+1) \frac{p^m(1-p)^{M-m}M!}{m!(M-m)!}$$

$$n_{av}^2 = Np \sum_0^M (m+1)P_m'$$

$$= Np\left[\sum_0^M P_m' + \sum_0^M mP_m'\right]$$

$$= Np[1 + Mp]$$

or

$$n_{av}^2 = Np[Np + (1-p)] \quad (6)$$

where P_m' refers to a different total M rather than N.

The quantity $u = n_{av}$ is the mean value for the number of counts expected from the measurement. It is also of interest to determine the amount by which any given measurement may be expected to deviate from the mean value. The quantity σ used to denote this is called the "standard deviation" and σ^2 the "dispersion" of the distribution. σ represents the "root mean square" deviation.

$$\sigma^2 \equiv \sum_0^N (n-u)^2P_n \equiv u^2 \sum_0^N P_n$$

$$- 2u \sum_0^N nP_n + \sum_0^N n^2P_n$$

or

$$\sigma^2 \equiv (n_{av}^2 - u^2) \quad (7)$$

from the definitions of n_{av}^2 and u. This result is quite general! For the Bernoulli problem (equation 3)

$\sigma^2 = u(1-P)$ or

$$\sigma = \sqrt{u(1-p)} \quad (8)$$

This shows that if p is small, the standard deviation is equal to $u^{1/2}$. Thus if 100 counts are expected on the average, the actual value of a given count has a good chance of differing from this by about ± 10 or 10%, whereas for 10^6 counts the deviation is $\sim 0.1\%$. If p is near unity, $\sigma \ll u^{1/2}$. This will happen for counting only when a short-lived radioactive material is counted over several half-lives and with high ($\sim$ unity) detection efficiency. The significance of the decreased uncertainty from $u^{1/2}$ is that now most of the active atoms originally present are counted and are not just a small sample. In the limit where all of the atoms are counted, there is no uncertainty as to how many were originally present. This situation is unusual since p is usually extremely small because of a combination of the factors involved in its definition.

Poisson Distribution

When p is very small and N is very large and $n \ll N$, equation 3 becomes simplified by the substitutions $N(N-1)(N-2) \ldots (N-n+1) \approx N^n$, $(1-p)^{N-n} \approx e^{-p(N-n)} \approx e^{-u}$, and $p^nN^n = u^n$ giving

$$P_n \approx u^n e^{-u}/n! \quad (9)$$

which is known as the "Poisson" distribution. This distribution is much more general than equation 3 since, as is shown below, it may be derived with-

out assuming that p is the same for each atom.

General Statement of Problem

The derivation of equation 9 may be made very general using the law of large numbers. The original statement of the counting problem required a constant probability p for all atoms. In general, there is a certain probability (which is usually zero) that any given atom in the universe will disintegrate and be detected by producing a count in the counter during the measuring interval. The general problem may thus be expressed as below.

If p_i represents the probability that the ith atom in the universe will produce a count during the measuring interval, what is the probability P_n that exactly n counts will be obtained?

Assume that $p_i \ll 1$ and $np_i \ll 1$ in general and let

$$u \equiv \sum_i p_i \qquad (10)$$

The derivation of the general term P_n may be understood more readily by considering P_0, P_1, etc., first. The probability that *no* counts are obtained is the product of the separate probabilities $(1 - p_i)$ that each atom shall give no count. Thus

$$P_0 = \mathcal{P}_i (1 - p_i) \approx \mathcal{P}_i e^{-p_i} = e^{-\sum_i p_i}$$

$$= e^{-u}$$

(where $\mathcal{P}_i$ means the product of terms for all values of i).

The probability P_1 of just one count is obtained by an extension of the reasoning for P_0 similar to the introductory problem 4 above.

$$P_1 = \sum_j \frac{p_j}{(1 - p_j)} \mathcal{P}_i (1 - p_i)$$

$$= e^{-u} \sum_j \frac{p_j}{(1 - p_j)} \approx e^{-u} \sum_j p_j = ue^{-u}$$

The term p_j above is the probability that the jth atom will give an effect and the term $(1 - p_j)^{-1} \mathcal{P}_i (1 - p_i)$ is the probability that all of the rest do not. In the sum, each term has the factor $(1 - p_j)^{-1}$. Since $p_j \ll 1$, negligible error results from omitting this factor.

The probability P_n may be obtained by reasoning similar to that for illustrative problems 5 and 6 above.

$$P_n = \frac{1}{n!} \sum_{a_1, \ldots a_n} \left[\frac{p_{a_1}}{(1 - P_{a_1})} \cdots \right.$$

$$\left. \frac{p_{a_n}}{(1 - p_{a^n})} \right] \mathcal{P}_i (1 - p_i) \qquad (11)$$

where a_1, a_2, etc. are n independent subscripts similar to i and j above. If $np_i \ll 1$ also, we can neglect the $(1 - p)$ terms in the first part of the above expression to obtain

$$P_n \equiv P_n(u)$$

$$= \frac{e^{-u}}{n!} \sum_{a_1} p_{a_1} \sum_{a_2} p_{a_2} \cdots$$

$$\sum_{a_n} p_{a_n} = \frac{p^n e^{-u}}{n!} \qquad (9)$$

The significance of the separate terms in equation 9 are now apparent. e^{-u} is the probability that *all other* atoms do *not* give a count. $n!$ is the "arrangement" factor as discussed in problem 5 above. p^n represents the products of the separate $\sum_i p_i$ terms for each of the n chosen atoms. Actually equation 11 should omit the terms in each sum corresponding to the particular atoms selected by the preceding sum terms (see problem 5). For $np_i \ll 1$ or $np_i \ll u$, this neglects relatively few terms in the infinite sums to give negligible error, and it greatly simplifies the expression of equation 11.

Properties of Poisson Distribution

Since the Poisson distribution (equation 9) has been shown to apply quite generally to counting problems involving small sampling (i.e., $p_i \ll 1$ and $np_i \ll 1$), it is of interest to derive some of the properties of this distribution

similar to those of equations 4–8 for equation 3.

$$\sum_0^\infty P_n = e^{-u} \sum_0^\infty \frac{u^n}{n!} = e^{-u}e^{+u} = 1 \qquad (12)$$

$$n_{av} \equiv \sum_0^\infty nP_n = e^{-u} \sum_0^\infty n \frac{u^n}{n!}$$

$$= e^{-u} \sum_1^\infty \frac{u^n}{(n-1)!}$$

$$= ue^{-u} \sum_0^\infty \frac{u^m}{m!}$$

or

$$n_{av} = u \qquad (13)$$

as expected.

$$n_{av}^2 \equiv \sum_0^\infty n^2 P_n = e^{-u} \sum_1^\infty \frac{nu^n}{(n-1)!}$$

$$= ue^{-u} \sum_0^\infty \frac{(m+1)u^m}{m!}$$

$$n_{av}^2 = ue^{-u} \left[\sum_1^\infty \frac{u^m}{(m-1)!} + \sum_0^\infty \frac{u^m}{m!} \right] = ue^{-u} \left[u \sum_0^\infty \frac{u^s}{s!} + \sum_0^\infty \frac{u^m}{m!} \right]$$

or

$$n_{av}^2 = u^2 + u \qquad (14)$$

Using equation 7, we obtain $\sigma^2 = u$ or

$$\sigma = u^{1/2} \qquad (15)$$

as for the Bernoulli distribution when $p \ll 1$.

Inverse Problem for Counting

The result of the direct problem, as given by equation 9, may be written

$$P_n(u) \equiv u^n e^{-u}/n!$$

showing that it is a function both of n, the number of counts actually received, and of $u \equiv \sum_i p_i = n_{av}$, the mean-expected-number of counts. In actual practice, when counting, the directly measured quantity is n and the desired quantity is u. The inverse problem may be stated thusly: For an actual count n, what is the probability that the actual value of u lies between u and $(u + du)$? The philosophical justification for such a question lies in the assumption that, in principle, the experiment can be repeated as many times as desired to obtain u with any desired accuracy by increasing the total volume of data. A little thought will show that equation 9 is also the solution of the inverse problem when written

$$P_n(u)du = u^n e^{-u} du/n! \qquad (16)$$

It should be noted that n is constant and u variable in equation 16 while u was fixed and n variable in equation 9. Also n is variable only in integer steps while u is continuously variable.

The properties of equation 16 may be examined as were equations 3 and 9.

$$\int_0^\infty P_n(u)du = \frac{1}{n!} \int_0^\infty u^n e^{-u} du$$

$$= \frac{n!}{n!} = 1 \qquad (17)$$

$\int_0^\infty x^n e^{-x}\, dx$ is a definition of $n!$ for all values of n (gamma function). This may be seen by performing successive integrations by part. This shows exactly unit probability that u has *some* value.

$$u_{av} \equiv \int_0^\infty uP_n(u)du$$

$$= \frac{1}{n!} \int_0^\infty u^{n+1} e^{-u} du = \frac{(n+1)!}{n!}$$

$$= (n+1) \qquad (18)$$

This result (that the mean expected value for u is larger than n) is unexpected at first but may be easily understood from a simple example. Thus, if $n = 0$, it is clear that u is not necessarily also zero; therefore u_{av} cannot be zero. Note, by contrast, that if $u_{av} = 0$, then $n = 0$ is the only possible result.

The most probable value u_0 of u is the maximum of equation 16

$$0 = \frac{d}{du}P_n(u) \qquad \text{gives} \qquad u_0 = n \quad (19)$$

This result shows that the most probable value of u is the measured value n. Similarly

$$u_{av}^2 \equiv \int_0^\infty u^2 P_n(u)du = \frac{(n+2)!}{n!} = u_{av}(u_{av}+1) \quad (20)$$

and

$$\sigma^2 = u_{av} \qquad \text{or} \qquad \sigma = u_{av}^{1/2} = (n+1)^{1/2} \quad (21)$$

This result is similar to equation 15 except that $(n+1)$ is used instead of u. If $n \gg 1$, the distinction between n and $(n+1)$ is not important.

Gaussian Distribution

Information concerning the shape of equation 9 is obtained by examining the ratio of the nth term to the preceding term

$$\frac{P_n}{P_{n-1}} = \frac{u}{n} \quad (22)$$

This shows that P_n increases with n for $n < u$ and decreases with n for $n > u$. For $n \gg u$, the terms decrease very rapidly with n since each term is only a small fraction of the preceding one. Similarly, for $n \ll u$, the terms rapidly decrease in size as n is decreased. From equation 22, the maximum occurs for $n = u$; therefore $P_u = P_{u-1}$ are the maximum values. The function P_n thus has a flat maximum near P_u and drops off rapidly on either side. Most of the area of a plot of P_n vs n occurs between $(u-\sigma)$ and $(u+\sigma)$ where $\sigma = u^{1/2}$ from equation 15. The value of P_u is obtained in a convenient form by replacing $n!$ by use of Stirling's formula

$$n! \approx (2\pi n)^{1/2}(n/e)^n \quad (23)$$

giving

$$P_u = u^u e^{-u}/u! = (2\pi u)^{-1/2} \quad (24)$$

When $u \gg 1$, it is customary to evaluate the probability P_n by assuming that a Gaussian or error-type distribution function applies. When suitable approximations are made, it is possible to express equation 9 as a Gaussian function as shown below. To do this, we use

$$x \equiv (n-u) \quad (25)$$

as the fundamental variable and let $f(x) \equiv P_n$ define $f(x)dx$ = probability for x to lie between x and $(x+dx)$. Although it does not influence the result, we shall assume below, for convenience, that x is positive.

$$f(x) = P_{u+x} = \frac{u^{u+x}e^{-u}}{(u+x)!} = P_u(u/u+1)(u/u+2)\cdots(u/u+x)$$

We consider only the cases where $|x| \ll u$

$$f(x) = (2\pi u)^{-1/2}[(1+1/u)(1+2/u)\cdots(1+x/u)]^{-1}$$

Since $x \ll u$ we may use $(1+x/u) \approx e^{x/u}$ to give

$$f(x) \approx (2\pi u)^{-\frac{1}{2}} e^{-\frac{1}{u}(1+2+\cdots+x)} \approx (2\pi u)^{\frac{1}{2}} e^{-\frac{1}{u}\int_0^x x dx}$$

or

$$f(x) = (2\pi u)^{-1/2}e^{-x^2/2u} = (2\pi\sigma^2)^{-1/2}e^{-\frac{1}{2}(x/\sigma)^2} \quad (26)$$

This is the commonly-used Gaussian or error function which shows that $f(x)$ decreases rapidly for $|x| > \sigma$. It is customary to let $t = x/\sigma$ be the variable to give

$$\phi(t)dt = f(x)dx = (2\pi)^{-1/2}e^{-t^2/2}dt \quad (27)$$

which is independent of σ.

The inverse problem, with equation 16 as the solution, may also be expressed approximately by a Gaussian distribution when $n \gg 1$ and $|u-n| \ll n$. Let $y = (u-n)$ and

$$f_n(y)dy = \frac{u^u e^{-u}dy}{n!} \approx \left(\frac{e}{n}\right)^n \frac{u^u e^{-u}dy}{\sqrt{2\pi n}} = \left(\frac{n+y}{n}\right)^n \frac{e^{-y}dy}{\sqrt{2\pi n}}$$

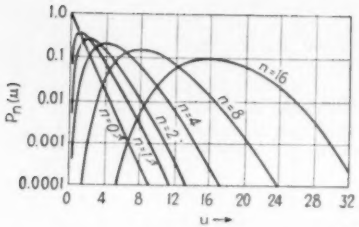
$$\ln\left(\frac{n+y}{n}\right)^n = n\ln\left(1+\frac{y}{n}\right) = n\left[\frac{y}{n} - \frac{1}{2}\left(\frac{y}{n}\right)^2 + \cdots\right] \approx y - \frac{y^2}{2n}$$

So

$$f_n(y)dy \approx (2\pi n)^{-1/2}e^{-y+y-y^2/2n} = (2\pi n)^{-1/2}e^{-y^2/2n} \quad (28)$$

which corresponds to equation 26.

The behavior of $P_n(u)$ is not sym-



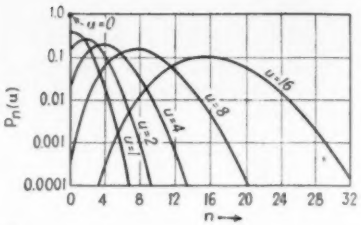


FIG. 1.

If u is the mean expected result for a count, then $P_n(u)$ is the probability that exactly n counts will actually be obtained.

If n counts are actually obtained, then $P_n(u)du$ is the probability that the true mean is between u and $(u + du)$.

metric in n and u except to the degree that both can be approximately expressed as Gaussian distributions for u and n large and $|u - n| \ll u, n$. In Fig. 1, $P_n(u)$ has been plotted as a function of n for $u = 0, 1, 2, 4, 8, 16$ and as a function of u for $n = 0, 1, 2, 4, 8, 16$. A logarithmic scale is used for the ordinate which should give the curves a parabolic shape if the Gaussian distribution were to apply rigorously. In Fig. 2, the Gaussian distribution, equation 27, is plotted in a similar fashion (curve A).

Finite Resolving Time

All apparatus for the detection of individual particles have finite resolving times such that particles which are spaced too closely will not give separate counts. This insensitive period, which occurs after the detection of one particle and before the system can respond properly to the next particle, is due either to the detection device itself (Geiger counter, proportional counter, ionization chamber, etc.) or to the associated amplifier circuit, level-setter circuit, scaling circuit, ratemeter circuit or mechanical register. When accurate information concerning input rates is desired, it is necessary to correct for the counts lost in this fashion.

The following discussion applies to Geiger counters and to the other detection devices.

Since the theory of Geiger counter action will be discussed in considerable detail in a following paper of this series, for the present purpose, it is sufficient to say that the discharge in the counter forms a positive ion "sheath" about the central wire, which extinguishes the discharge. The counter is then unable to respond to a new ionizing event until this positive ion "sheath" has almost reached the outer cylinder. This process requires approx. 10^{-4} to 10^{-3} sec, depending on the dimensions of the counter and its gas contents. This represents a minimum insensitive period for the system. If a "slow" amplifier circuit is used, or if the following parts of the circuit give a longer insensitive time, the actual insensitive time may be much larger. This last fact is frequently overlooked and will be considered in a later article.

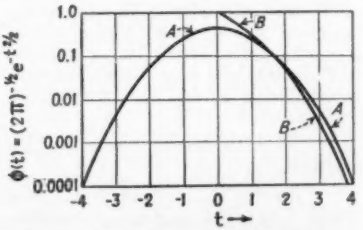


FIG. 2. Curve A shows the Gaussian or "error" function $\phi(t) = (2\pi)^{-1/2} e^{-t^2/2}$. For a large count, this gives the probability that the count will deviate from its mean expected value by t to $t+dt$ times the standard deviation of the count. Curve B shows the probability that the deviation exceeds t times the standard deviation.

It will also be shown in a future article that the Geiger counter counting loss is actually a complex function of the "input" counting rate even when fast circuits are used. In practice, the form of the dependence may be sensitive to the actual circuit parameters used. If the "regulation" of the high voltage and bias voltages as a function of counting rate is not good, then the circuit may count with relatively small losses up to a certain rate and block for higher rates. This type of behavior can be avoided, however, by proper circuit design, and a response similar to the idealized types discussed below can be obtained. Also when the theory of counting losses is developed, one of these idealized behaviors is assumed to apply.

Counting Loss Problem

Let the "input" counting rate N be the counting rate which would be obtained if the insensitive time were zero, and the "output" counting rate n be the rate when there is an insensitive τ after each output count. In this statement of the problem, it is assumed that a new input count coming during the insensitive time, $t \leq \tau$, after the previous output pulse, will not give an output pulse *and* also will *not* extend the insensitive time. A random input is always assumed. The problem is to find the relation between n and N.

Solution. The counting loss will be caused by those input counts which arrive during the insensitive periods. Since each output count has an insensitive time τ and there are n output counts per sec, on the average, the total insensitive time per sec is $n\tau$. The average number of input counts during the interval $n\tau$ is just $Nn\tau$, however, so the loss is $(N - n) = nN\tau$ per sec. This has the solutions:

$$N = n/(1 - n\tau) \qquad \text{and} \qquad n = N/(1 + N\tau) \quad (29)$$

This shows that the percentage loss is proportional to the output rate. The maximum output rate as $N \to \infty$ is just τ^{-1}. For a dead time $\tau = 10^{-3}$ sec, an output rate of 100 per sec gives a 10% counting loss, and the rate must be held to 10 per sec to have only a 1% counting loss. In practice, the counting rates used may be such that $\sim$1–20% counting losses are obtained in order to obtain a large total count in a short time for good statistical accuracy. The counting loss is then corrected by the use of equation 29, when τ has been previously measured.

A second common statement of the counting loss problem modifies the previous statement as follows. It is again assumed that a new input count arriving during the insensitive period will *not* be counted, but it is assumed that the insensitive time is *extended* by the amount τ after the (undetected) count arrives. Again, the relation between N and n is desired.

Solution. This problem is solved most readily by considering the case of a very high input rate. The system will remain blocked if the input counts are always spaced by less than τ. In general, another output pulse is obtained once *every time* the system recovers from blocking, i.e., every time a timing spacing $\geq \tau$ occurs between successive input counts. Thus, $n = N \times$ (probability of zero counts during the time τ after a given count). Since the mean number, u, of input counts expected during the time τ is $N\tau$, the probability that no counts be received in a given interval τ is, from equation 9, $P_0(N\tau) = e^{-N\tau}$ and

$$n = Ne^{-N\tau} \quad (30)$$

For $(N\tau)^2 \ll 1$, equations 29 and 30 both give approximately

$$n \approx N(1 - N\tau) \approx N(1 - n\tau) \quad (31)$$

For $N\tau \gg 1$, the output blocks as expected from the derivation. The maximum of equation 30 occurs for $N\tau = 1$ which gives $n = (\tau e)^{-1}$.

Equations 29 and 30 are extreme cases of single recovery processes. What often happens is something intermediate. Thus, the system may require a time τ_0 to recover enough to give another output pulse if there was a large spacing between the two preceding input pulses. However, the extension of the insensitive time τ after

a given input pulse may be less than τ_0 for shorter spacings of the two preceding input pulses.

The best way to solve the problem for a given counting system is to vary the input rate experimentally in small steps over a wide range of known (random) input rates and measure the output rates to obtain directly the actual shape of the output vs input rate curve. To do this accurately is a very tedious process, however, and the shape of the curve may vary somewhat with time. The usual process, therefore, is to assume that either equation 29 or 30 applies and restrict measurements to the region where they are both closely given by equation 31. This requires that $(N\tau)^2 \ll 1$.

Techniques for the experimental measurement of dead times will be discussed in greater detail in a forthcoming article of this series.

Scaling Circuit Regularizing Action

When the output from a system counting random pulses directly activates a mechanical register, a rate of only one count per sec will give a counting loss of 1 to 10% depending on τ. Since this high loss at moderate counting rates usually cannot be tolerated, it is customary to use a scaling circuit between the amplifier and the register circuits. A scale-of-m circuit is one which gives an output count for every m input counts. At present, the most common scaling circuit is derived from the basic scale-of-2 circuit giving scales of 2, 4, 8, 16, 32, 64, 128, etc. More recently, decimal type scales of 10, 100, etc., have been developed and may be used more frequently in the future. The relative advantages of each type will be discussed in a later section.

One obvious characteristic of a scale-of-m circuit is an average output rate slower than the input rate by the factor m. Another less generally understood action is the *regularizing effect* of the scaling circuit on the output. Thus, when random pulses are sent into a scale-of-128 circuit, the output pulses are quite uniformly spaced with only a small fractional variation in the spacings between successive output pulses. For a mechanical register with a resolving time of $\frac{1}{20}$ sec, there will be a loss of $< 0.1\%$ of the register counts when a scale-of-32 circuit is used with an *output rate* of 10 counts per sec whereas 5% of the counts would be lost for an output rate of only 1 count per sec without a scaling circuit. The use of a large scaling ratio thus decreases the output rate and also permits the average spacing of the output pulses to be only a little larger than the resolving time to give negligible counting losses. The theory of the scaling circuit regularizing action will be developed below.

A scale-of-m circuit is assumed to have a random input rate of Nm per sec corresponding to an output rate of N per sec. The resolving time of the scaling circuit is assumed to be negligible so counting losses other than those of the register are negleted here or are considered separately later. Thus, what is the probability, $q_m(x)$, that the actual timing spacing between output pulses lies between x and $(x + dx)$ where $x = Nt$ is the timing in units of the average spacing between output pulses? And what is the probability $Q_m(x)$ that the next output pulse will have arrived by $t = x/N$?

Solution. The circuit at the time $t = x/N$ will have n input counts where $n = 0, 1, 2, 3, \cdots \infty$. The probability that there is exactly a given number n may be expressed by equation 9. The *mean* number of input counts expected during the interval $t = x/N$ is just $u = Nmt = mx$. The next output pulse will have been obtained if $n \geq m$. The probability $Q_m(x)$ that this will have happened is just the total probability that $n \geq m$. From equation 9 this is

$$Q_m(x) = \sum_{m}^{\infty} P_n(mx)$$

$$= [1 - \sum_{0}^{m-1} P_n(mx)]\, dx \quad (32)$$

where $P_n(mx) = (mx)^n e^{-mx}/n!$. The probability that the next output pulse

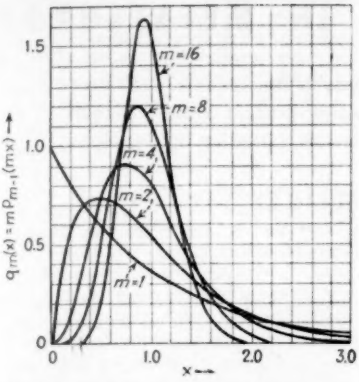


FIG. 3. This figure illustrates the regularizing action of a scale-of-m circuit with a random input. The curves show the probability that the timing spacing between two successive output counts will lie between x and $x + dx$ times the average spacing.

will arrive between x and $(x + dx)$ is $q_m(x)dx$ = increase in $Q_m(x)$ during dx.

$$q_m(x) = \frac{d}{dx} Q_m(x)$$

$$= \sum_{n}^{\infty} [mP_{n-1}(mx) - mP_n(mx)]$$

Thus $$q_m(x)dx = mP_{m-1}(mx)dx$$

$$= m \frac{(mx)^{m-1}e^{-mx}}{(m-1)!}dx \quad (33)$$

The probability distribution $q_m(x)$ of the timing spacings about the mean is thus the same as equation 16 for the inverse counting problem with order $(m - 1)$ rather than m. The distribution has already been shown to be normalized, equation 17, and to have a mean spacing $mx = [(m - 1) + 1]$ or $x = 1$ from equation 18. From equation 19, the most probable spacing is $mx = (m - 1)$ or $x = (1 - 1/m)$. The standard deviation of x, from equation 21, is σ of $mx = \sqrt{m}$ or σ of x is

$$\sigma \text{ for } x = m^{-1/2} \quad (34)$$

Thus, for a scale-of-64 circuit, the standard deviation of the spacings from their mean is $\frac{1}{8}$ of the value of the mean spacing. If the scaling factor m is not too small, the Gaussian distribution will approximately hold and Fig. 2 may be used. Curve B of Fig. 2 gives the probability that the actual spacing will deviate from the mean spacing by t times the standard deviation. Only deviations where the spacing is too small give counting losses, so half of the value from curve B should be used to calculate losses.

In Fig. 3, $mP_{(m-1)}(mx)$ is plotted as a function of x for $m = 1, 2, 4, 8$, and 16. These curves show directly the shape of the regularizing curves for scales of 1 (no scaling), 2, 4, 8, and 16. The curves are normalized so the probability for the next count to arrive during $x \leq x_1$ is just the area under the curve for $x \leq x_1$. Thus less than 1% of the counts will have arrived by $x = \frac{1}{2}$ for a scale of 16, and about 10% for a scale of 8. The small area of the curves up to small values of x for $m > 1$ is in strong contrast with $P_0(x)$ which corresponds to no scaling action. A study of Fig. 3 shows the great value to be gained by the use of even small scaling factors when the use of large scaling factors is considered to be too expensive.

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TRACER ISOTOPES IN METALLURGY

Survey of applications to the study of fundamental problems, oxidation, corrosion, metallography, process control, annealing, and analytical procedures—with extensive bibliography

By J. K. STANLEY

Research Metallurgist, Westinghouse Electric Corporation
East Pittsburgh, Pennsylvania

BOTH RADIOACTIVE AND STABLE isotopes can be used to advantage in metallurgy. The principle on which an isotope—whether stable or unstable—is used is as follows: When a minute amount of the isotope is added to some of its normally occurring isotopes, the mixture behaves experimentally as though it were homogeneous. Chemically the mixture is the same as before, and whatever happens to the normally occurring isotopes also overtakes the added isotope. Very small amounts of the added isotope are required.

With the addition of a radioactive isotope, radioactivity acts as an indicator of the behavior of the element under study. With the addition of stable isotopes the presence of abnormal ratios of the added isotope to the normally present isotopes serves as the indicator; if the relative proportions of the isotopes in the original mixture are known, the amount of material in the end product can be estimated from the new ratios found.

Stable isotopes must be concentrated before they can be used as tracers and accurate means must be provided for measuring the isotopic abundance ratios. It is generally sufficient to build up a relatively high concentration of one isotope over the major occurring isotope and to use the ratio of the two as an index of the progress of a reaction. The primary concern is not the absolute abundance ratio, but rather the changes in it.

Stable element isotopes are detected with mass spectrometers. The method, especially the preparation of the gaseous phases and detection of the ions, is laborious compared to the detection of radioactive isotopes. The limiting factors in research with stable isotopes at the present time are the scarcity of mass spectrometers, the limited number of trained personnel to operate and maintain them, and the meager supply of concentrated isotopic mixtures.

Very little work has been done in metallurgy with stable isotopes as tracers. Only one reference has been found which deals with stable isotopes and diffusion (*1*). On the other hand, there are several examples where radioactive materials have been used to advantage in metallurgy; these will be covered under appropriate sections.

Two characteristics of radioactive materials must be considered in applying them to metallurgical problems: One is the half-life and the other is the energy of the radiation. These characteristics are interrelated—in general, the longer the half-life the weaker the radiation, and vice versa. If the half-life is too short, its use for metallurgical studies may be limited. A reaction time may be longer than the half-life and the radioelement will have disappeared. Short half-lives also prevent storing or stock-piling. In another respect, however, short half-lives minimize dangers of long-lasting contamination.

The energy of the radiation is related to its intensity which must be sufficient to affect Geiger-Müller counters, electroscopes, photographic plates, etc. Most of the lower atomic weight radioactive elements are electron or

beta-ray emitters, the heavier elements are beta and/or gamma-ray emitters, and the heaviest elements, in addition to giving off beta and gamma rays, are also alpha-particle emitters. Very weak beta radiation must be picked up with specially designed instruments (*2*); for example, S^{35} (*3*) and C^{14} (*4*) must be followed by specially built Geiger counter tubes. For other elements, such as P^{32} and Na^{24}, ordinary Geiger tubes can be used.*

A large number of metals can be used for tracer studies since many of them have one or more radioactive isotopes with satisfactory half-lives and with radiation sufficiently intense to permit easy detection. Nonmetallic elements such as oxygen, nitrogen, hydrogen, carbon, sulphur and phosphorus are also of importance in metallurgy. Of these nonmetallic elements, however, no satisfactory radioactive isotopes are known for oxygen, nitrogen and hydrogen. This leaves C^{14}, S^{35}, and P^{32} for use as radioactive tracers.

Radioactive elements find their usefulness in two ways. In one way, the tagging of atoms enables one to follow the actual movement of the radioactive material. This constitutes what might be called the "true" use of radioactive elements. In another way techniques involving radioactivity measurements offer attractive features over some conventional methods of analysis or control in speed, cost, or increased accuracy.

The simplest method of using a radioactive element is to incorporate it into the system under study and to measure the distribution of the tagged element in the system. This is done either by counting or by photographic plates. The photographic method, known as autoradiography, consists of placing specimens containing radioactive materials in contact with the film for a given time and then developing the film.

In metallurgical reactions some of the greatest possibilities lie in the use of the "exchange reaction." This reaction can be illustrated by reference to Hevesy and Zachmeister's classical work (*6*) in 1920 on checking the Arrhenius theory of electrolytic dissociation. Solutions of normal lead chloride and lead nitrate containing a radioactive lead isotope, thorium B, were mixed. The two salts were then extracted from the mixture. After separation the salts were found to be equally radioactive indicating that there had been an exchange of lead ions. Had there been no interchange of lead ions, the Arrhenius theory would have suffered a severe setback.

This exchange reaction has been very helpful in giving the chemist information on the strength and nature of chemical bonds, the structure of compounds, and the kinetics of reactions. There is no good reason why the kinetics of metallurgical reactions from blast furnace to refining reactions or from roasting of ores to electrochemical procedures cannot be studied similarly.

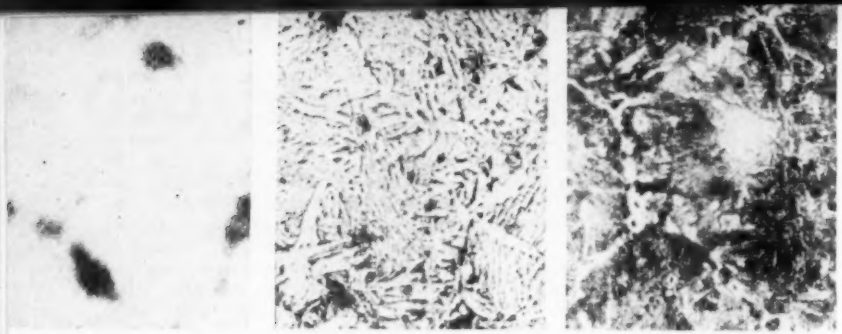
Hevesy (*7*) also realized that radioactivity measurements could be used for chemical analysis. One field of analytical procedure is the determination of minute quantities of materials in cases where the sensitivity of conventional methods is insufficient. The determination of small solubilities and low vapor pressures is often possible. Under optimum conditions, it is possible to detect 10^{-10} gram of a material.

Early Use of Tracers in Metallurgy

The earliest use of radioactive materials as tracers was, of course, limited to the naturally occurring elements. The first worker to recognize the use of these materials as scientific tools was Hevesy (*8*) in 1912. With F. Paneth (*7*) in 1913, Hevesy adapted the method to chemical problems. They showed that extremely minute quantities of lead (10^{-9} to 10^{-14} gram) could accurately be estimated in determinations of aqueous solubility of lead sulphide and chromate.

Almost at the same time, the first work was done in metallurgy when

* Many radioisotopes can be prepared at institutions having cyclotrons. Mattauch and Fluegge (*5*) give the nuclear reactions for preparing radioisotopes. See NUCLEONICS, September, 1947, for information on radioisotope availability.



Autoradiograph showing outlines of austenite grain boundaries

Etched with HNO_3 to show ferrite and pearlite

Etched with Oberhoffer's etch to reveal austenite. Compare with autoradiograph

Simultaneous determination of austenite grain size (primary structure) and transformation structure, pearlite and ferrite (secondary structure). Magnification ×60.

Groh and Hevesy (*9*) determined the selfdiffusion* of molten lead. A layer of lead rendered active with the radioactive isotope of lead, thorium B, was placed at the bottom of a tube and above it a layer of common lead. The lead was melted and held at 340° C for several days. Afterwards the cylinder was sectioned, the concentration of thorium B in various positions was determined by measuring the α rays, and thus the selfdiffusion of molten lead was demonstrated.

In a similar manner both the selfdiffusion of lead in the solid state (*10*) and the diffusion of lead in the compound lead chloride (*11*) were carried out. More work was done later on the selfdiffusion of lead (*12, 13, 14*) and on the selfdiffusion of bismuth (*15*). The diffusion of radioactive lead in a gold-lead alloy was measured by Seith and Keil (*16*). A summary of these works by Hevesy is available (*17*).

Surface migration is another important aspect of diffusion. Schwartz (*18*) has shown that if polonium is deposited on silver foil at one end only and the temperature is raised to 300° C, a diffusion of the polonium along the silver can be noted by radioactive measurements. No volume diffusion takes place up to 500° C; this is an interesting commentary upon the relative ease with which surface and volume diffusion occur.

In another direction Tammann and Bandel demonstrated the use of the autoradiographic method for studying many metallurgical problems (*19, 20*). Using the radioactive lead isotope, thorium B, as an addition to various metals, they were able to study primary crystallization, segregation, partition between two materials, inclusions, recrystallization, grain growth and cold-work. Some examples from their work are worth mentioning. Perhaps the most important results which Tammann and Bandel obtained were in connection with phase transformation recrystallization, and grain growth. Using the autoradiographic method on steel in conjunction with etching, they showed that one can simultaneously observe the prior austenitic grain size and the resultant pearlitic transformation.

In the formation of the primary

* The term *selfdiffusion* is self-explanatory and applies here to both the liquid and solid state, although the term is most often used in connection with the solid state. Selfdiffusion, refers to the movement of atoms in a liquid composed of identical atoms or to an interchange of atoms from site to site in a crystal lattice.

structure of the steel, the austenite grains were developed by forcing insoluble lead-containing thorium B to the grain boundaries, where it stayed because of its low diffusibility and remained there unaffected by the subsequent transformation. This radioactivity was measured on a photographic plate in the matter of an hour, and gave an outline of the original austenitic grain size. On the same section, etching brought out the transformation products, pearlite and ferrite.

This circumstance is illustrated in the photographs on the left. The left figure shows the austenite grain size determined by the autoradiographic method, the center figure shows the ferrite and pearlite obtained by etching, while the figure on the right is the Oberhoffer etch ($SnCl_2$, $CuCl_2$, $FeCl_3$, HCl) for revealing the austenitic grain size. The Oberhoffer etch, like other etches or procedures for revealing austenitic grain size, does not always work, so that determination of the primary structure is a major problem.

In recrystallization of cadmium, tin and zinc, in which thorium B is incorporated, Tammann and Bandel found that the initial grain structure is outlined by the deposition of radioactive grain boundary material. This grain boundary material remains in spite of later grain structure changes involving recrystallization by heating after cold-work.

Grain growth, known as *coalescence*, in a cast structure or in a recrystallized wrought material can also be studied. The original grain structure is outlined by the thorium B and it becomes possible to compare the final grain structure with the initial structure. Much fundamental information can be obtained using this technique.

The current interest in leaded steels for free-machining can be investigated using thorium B to determine the distribution of lead, for example, in various sections of ingots.

Werner (*21*), by measuring the radiation from the radium isotope, Th X, studied changes in cold-working and recrystallization in Zn, Tl and Al. He was able also to detect a change in the crystal structure of Tl by this method.

Artificial Tracers in Metallurgy

After their discovery in 1934, work with artificial tracers in metallurgy was slow in getting started. It is accelerating now, however, as the possibilities of the method become known and as tracer elements become available.

The field for metallurgical study can be divided into three groups according to the type or nature of the work to be done. One division includes experiments of a fundamental or theoretical nature such as diffusion and exchange reactions. Another includes experiments for working out processes or techniques which, if once worked out, would require no further use of tracers. The third and last field might cover analytical procedures.

There are many obvious uses to which tracer elements may be put. Many of the following suggestions will no doubt be tried. Less obvious applications certainly can be developed for specific problems; such work of course will depend upon the ingenuity of the worker. Many of the studies suggested might be considered as fields for the physicist interested in the solid state. While this may be true to some degree, there is no reason why the metallurgist should not make use of these methods, particularly in strictly metallurgical fields.

The following outline gives some idea of the scope of the new approach to the study of metallurgical problems.

FUNDAMENTAL STUDIES

Diffusion

An ideal problem in which to use artificial tracers, as already mentioned, is selfdiffusion. This field was opened up by Hevesy and co-workers in 1920 (*9*, *10*), using, of course, the naturally radioactive materials. Since 1934, many experiments have been carried out on selfdiffusion. The selfdiffusion of Au (*22*, *23*), Cu (*24–27*), Zn (*28*, *29*), and Ag (*30–32*) has been studied.

Two techniques have been used:

1. A thin layer of radioactive metal is deposited on the solvent metal and after an annealing treatment the decrease in surface activity caused by the diffusion of the radioactive atoms inward is determined with Geiger counters.
2. Radioactive material is deposited on the solvent metal. After heat treatment, layers are cut on either side of the interface, the activity of each is measured, and a concentration-penetration curve is obtained which is then mathematically analyzed.

The selfdiffusion of a metal in a solid solution alloy was determined by Johnson (*33*). He studied the diffusion of radioactive silver and radioactive gold in an alloy containing 49.2 atom % gold and 50.8 atom % silver.

In spite of the great amount of work done on selfdiffusion, the mechanism of diffusion is not well understood, *i.e.*, movement of atoms from site to site in a crystal lattice. Is it by the presence of lattice site vacancies or by cyclic interchange?

The mechanism of many important metallurgical phenomena is dependent upon selfdiffusion. Annealing phenomena such as recrystallization, grain growth, and the crystallographic transformation of elements or solid solutions are essentially selfdiffusion phenomena.

The formation and growth of recrystallization nuelei depends on selfdiffusion. Grain growth or coalescence is the enlargement of grains from an initially fine-grained matrix. The transformation, for example, of α to γ iron on heating, or vice versa on cooling, is strictly a selfdiffusion phenomenon by the process of atoms shifting position.

Experiments might also be designed to show the differences between crystal and grain-boundary diffusion, as well as surface and volume diffusion.

It is also by the study of selfdiffusion that the mechanism or mechanisms of diffusion in commercial processes will be elucidated, processes such as carburization, nitriding, chromizing, calorizing (diffusing of aluminum), sherardizing (diffusing of zinc), siliconizing, bimetal production, powder-metallurgy sintering, and cladding.

The diffusion coefficients of elements which are sparingly soluble in others, such as Ti, Si, Ni, and Fe in aluminum might be determined conveniently by the tracer method. The important problem of diffusion of carbon in α iron is now being attacked in several laboratories by the radioactive method. In the illustrations given here, conventional analytical techniques could be used to determine the diffusion coefficients, but the methods are tedious, sometimes new ones have to be developed, and difficulties increase with decreasing concentrations—a situation not true when tracer elements are used.

Oxidation and Corrosion

The oxidation of copper has been studied by the tracer method by Bardeen, Brattain, and Shockley (*24*). A thin layer of radioactive copper first was electroplated on a copper specimen. The specimen was then oxidized for 18 minutes at 1000° C and a layer of oxide 1.25×10^{-3} cm was formed. The specimen was quenched after oxidation and the layers were removed chemically after which the activity of the copper surface was measured. The experiment showed that the ideas of Wagner (*35*) on oxidation were supported, namely, that the oxide grows by formation of vacancies in the copper lattice from the outer surface into the metal into which the copper ions diffuse.

There appears to be no reason why a similar experiment could not be performed with radioactive iron Fe^{59}. The study of oxidation-resistant alloys could be promoted by studying, first, the distribution of chromium using radioactive Cr^{51}, and then the distribution of the iron using radioactive Fe^{59}.

The study of corrosion using radioactive iron is also a possibility.

Metallography

The nature of the brittleness in steel due to high sulphur and high phosphorus

might be studied by the combined autoradiographic and conventional etching methods to see how these elements distribute themselves within the grain or grain boundary.

The identification of phases perhaps could be facilitated if one component were made radioactive. Considerable research is necessary in this field because the autoradiographic method must be improved to give better resolution before much can be accomplished in metallography.

Wear

Wear, including such factors as the influence of pressure, hardness, lubricants, similar and dissimilar metals, can be studied readily (*36*, *37*). In the general problem of wear, the sliding surfaces tear out minute particles on one surface and deposit them on the other. This exchange may take place to such extent that surfaces "seize" (weld together). If one surface were coated with a radioactive isotope and were then worked against the other, unactivated surface, extremely minute amounts of radioactive material would be transferred. This transferred material can be readily detected with Geiger counters and often radiographs of the initially unactivated surface can be made to show the nature of the pickup.

PROCESS CONTROL

Steel Making

Tracer techniques are also being extended to process metallurgy, *i.e.*, the study of chemical reactions.

In the study of phosphorus equilibrium in steel, Winkler and Chipman (*38*) added radioactive phosphorus to their laboratory melts and determined by counters the time requir_d for the slag-metal system to come to equilibrium after disturbances, such as making additions and temperature changes, had taken place. At 1608° C, the system under study reached equilibrium 15 minutes after a temperature disturbance. Once this equilibrium time was found, the use of radioactive phosphorus was discontinued.

Ingot practice might be followed by studying the segregation of carbon, sulphur and phosphorus in the ingots by the autoradiographic technique. The ingot could be sectioned and then a photographic film put up against the ingot and exposed for a certain length of time. On development of the film, the segregation of the radioactive element should be detectable.

An experiment such as this might be devised: A ladle of ordinary metal is teemed into a series of three molds. Into the first, some radioactive phosphorus is added; to the second, some radioactive sulphur; and to the third, some radioactive carbon. The three films could then be prepared and distribution of P, S, and C in the particular analysis of metal demonstrated.

C^{14} and S^{35} give off rather low-energy electrons of 0.145 Mev and 0.120 Mev, respectively. The energy of these electrons is about as low as one can use to affect a photographic plate, but with proper exposure time and type of emulsion, the radiation from C^{14} or S^{35} can be detected. P^{32} has a higher energy ray, namely 1.69 Mev, and readily affects a photographic plate.

Of course, the segregation of carbon, sulphur and phosphorus in ingots can be made by tedious and expensive point-to-point chemical analysis, but the autoradiographic method is simple and gives a complete picture of segregation of the element in question.

In the open hearths, which are gas- or oil-fired, there is the possibility of sulphur pickup from the fuel. To determine how objectionable sulphur in the fuel really is, radioactive sulphur would have to be used in the fuel to see how much of it is picked up by the slag and metal.

The distribution of alloying elements between metal and slag is also possible; for example, the conditions under which Cr remains in the iron or starts entering the slag can be determined by measuring the activity of the slag and metal at various intervals.

The observation of distribution and identification of inclusions might be facilitated by the addition of radio-

active isotopes of such inclusion forming elements as calcium (Ca^{45}) or titanium (Ti^{51}) to a slag-metal system. After removal of the slag and pouring of the metal, the resulting ingot would be sectioned for analysis by the autoradiographic method.

Annealing

In ferrous and nonferrous castings, in which cored structures are often present, a radioactive element of one constituent of the alloy would give rise to blackening on the photographic plate corresponding to cored or uncored areas, depending on which alloying element contained the radioactive element. The effect of time of annealing would demonstrate the destruction of the cored structure by giving uniform blackening to the photographic plate. Once the time and temperature of annealing were established, the use of radioactive tracers could be discontinued.

A check might be kept on controlled atmospheres. In the heat-treating of steel using combusted gases for a neutral atmosphere, some of the CO or CH_4 might be made with radioactive C^{14}. The inlet gas, and then the exhaust gas, would have to be checked for radioactivity by measurement. If the radioactivity of the exhaust gases were the same as the inlet gas, the atmosphere would be neutral; if the radioactivity were less, the atmosphere would be carburizing.

Another experiment along the same lines could check decarburization. A steel sample containing some C^{14} could be put into a furnace with the charge. If the atmosphere were decarburizing, some radioactivity could be detected in the exhaust gases; if it were neutral, no radioactivity would be detected. The two procedures, of course, could be combined.

ANALYTICAL PROCEDURES

Steel Analysis

Radioactive elements offer, in many cases, a rapid, accurate and inexpensive method of analyzing constituents in metallurgical processes, often while the process is going on. The determination of phosphorus in the basic open-hearth is an illustration (*39*). The method of analysis is relatively simple. The accuracy of conventional analytical methods generally decreases as the amount of the element in question decreases. With tracer methods, this is not the case, and the same degree of accuracy is obtainable from the lowest to the highest concentrations measurable.

There exists the possibility of keeping a continuous check on the distribution of phosphorus, and possibly sulphur, between the slag and metal in the basic open-hearth or other steel manufacturing methods. Such continuous check, while steel is being made, is possible, but difficult, by conventional means, whereas the radioactive method can be rapidly carried out. Thus purification of the steel can be followed right at the furnace.

The analysis of phosphorus in the metal would be carried out as follows: A small amount of radioactive phosphorus, P^{32}, is added to the bath as ferro-phosphorus; about 0.15 millicurie* of radioactive phosphorus per ton of steel is sufficient to give a counting rate of ten counts per second on a Geiger counter of 1⅛ in. sensitive tube length. The phosphorus atoms become rapidly distributed so that the ratio of normal phosphorus to the radioactive form is the same everywhere.

As the phosphorus goes into the slag, the percentage of the element in question can be determined by the measurement of the radioactivity of samples taken at various intervals. The first sample of steel taken is drawn off, its phosphorus content determined chemically, and the radioactivity of the sample noted. While the first chemical determination may take one and a half hours, this is still sufficient time for the radioactive method to be useful, inasmuch as the refining period is roughly half of the time (10–12 hours) required to make an open-hearth heat.

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*One millicurie is defined as 3.7×10^7 disintegrations per second.

The relation between radioactivity and concentration therefore is established in this way. Thereafter, identical samples are taken, and their radioactivity is measured. Since the relation between radioactivity and concentration is known, the per cent of phosphorus is readily calculated. Such determinations should not take more than three or four minutes after the sample is prepared.

S^{35} and C^{14} could conceivably be analyzed in the same way as phosphorus, but specially designed counters would have to be used because of the low energy of the β radiation of these elements.

Detection of Traces of Impurities

Traces of elements occurring as impurities can sometimes be determined by converting the impurity into a radioactive material in a cyclotron and measuring the nature of the radiation (*40*). Gallium in iron and copper in nickel have been determined in this way.

The so-called "modification" of high-silicon aluminum-silicon alloys is carried out by the addition of sodium as the modifier. Methods might be set up for accurate analysis of the amount of sodium required to carry out the modification.

Conclusion

From the above survey it may be concluded, that, while the literature on the use of radioactive tracers in metallurgy is not yet very extensive, it is sufficient to show that tracers may become important tools in this field as soon as metallurgists become acquainted with their use.

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NUCLEONIC EVENTS

BRITAIN TO BUILD ATOMIC ENERGY PLANT

Construction work on Britain's first atomic energy plant is scheduled to start shortly at Sellafield, Westcumberland, in a relatively isolated location in the lake district on the west coast of England.

The plant is primarily intended for the production of fissionable material in a chain-reacting pile. It is the second link in Britain's atomic energy projects. The first is the production of pure uranium from pitchblende concentrates at the Ministry of Supply's factory at Springfields, near Preston.

Britain's first experimental pile, the research establishment set up last year at Harwell, Berkshire, went into operation in mid-August. It is a low-power apparatus using a carbon moderator and is said to be similar to the first pile built in 1942 at Chicago and still operating there. This pile will be used for research on pile characteristics and possibly for the manufacture of radioactive isotopes.

A second higher-powered pile is scheduled for completion next year at Harwell. This is expected to be comparable to the experimental pile at Oak Ridge which produces the present U. S. supply of radioisotopes.

FAST-NEUTRON PILE OPERATING AT LOS ALAMOS

The existence of a nuclear reactor which uses plutonium instead of uranium as its fuel, employs fast neutrons, and operates without a moderator has been revealed by the Atomic Energy Commission. This new pile has been running at Los Alamos since last November.

Essentially a controlled, fast-neutron reactor, this pile has been operated at a rate of only a few hundred watts. With an expected increase in the rate at which heat is carried off, the power level will also be raised.

Reactors built during the war for other than direct use on bombs operated on natural uranium containing a small percentage of the fissionable U^{235} isotope. The number of neutrons absorbed in the nonfissioning uranium was of such a magnitude that difficulty in maintaining the reaction was encountered. With the necessity for slowing the neutrons down to their most effective speed by a carbon or heavy-water moderator, few remained for production of isotopes or manufacture of additional fissionable material. In addition, the slow-neutron reactor required hundreds of tons of uranium and moderator.

By contrast, the new fast-neutron reactor, consuming almost pure plutonium, requires only a comparatively few pounds of material. Because there are few nonfissionable materials to absorb fast neutrons, the "flux density" is high, that is, there are plenty of spare neutrons.

It has been said that, since it permits study of the fast-neutron chain reaction used in the bomb, the new pile was installed at Los Alamos primarily for the study of bomb physics.

PAPERS PRESENTED AT CANCER CONGRESS

The Fourth International Cancer Research Congress was held last month in St. Louis, Mo. Among the many papers presented were the following:

"Problems in Production, Distribution and Use of Isotopes," by Paul C. Aebersold; "The Possible Carcinogenic Effect of the Hiroshima and Nagasaki Atomic Bombs," by Shields Warren; "Quantitative Aspects of Radiation Carcinogenesis," by Austin M. Bures; "Uptake of Radioactive Phosphorus in the Phospholipid Fraction of Mouse Epidermis Undergoing Carcinogenesis by Methylcholanthrene," by C. J.

Costello, C. Carruthers, M. D. Kamen, and R. L. Simoes; "Metabolism of Radio-Iodo-Estradiol in Normal and Tumor-Bearing Mice," by S. Albert, J. Cohen, R. D. H. Heard, and C. P. Leblond; "A Technique for the Study of Connective Tissue Reactions to Radiation," by Benjamin Jolles.

Radiation therapy — "Recent Developments in High Energy Radiation Generators," by D. W. Kerst; "Production and Characteristics of a Fast Electron Beam," by L. S. Skaggs; "The Principles of Fast Electron Therapy in Cancer," by E. M. Uhlman; "Physical Research Studies Relating to a New Expanding Type of Cervical-Vaginal Radium Applicator," by E. C. Ernst; "Intrinsic Carcinoma Larynx; Classification and Technique of Teleradium Treatment," by M. Lederman; "Methods of Determining Distribution of Dose of Radiation in the Patient," by L. F. Lamerton; "The Results of Research in Transvaginal Roentgentherapy of Carcinoma of the Cervix," by Juan A. Del Regato; "Biological Effect of High Energy Roentgen Rays," by H. Quastler; "The Role of Surgery and Interstitial Radon Treatment in Cancer of the Superior Sulcus of the Lung," by J. Samuel Binkley.

Radiation—Carcinogenic—"Carcinogenic Action of Gamma and X-Rays," by E. Lorenz, A. B. Eschenbrenner, W. E. Heston, and Margaret K. Deringer; "Factors of Induction of Ovarian Tumors by X-Rays: Types, Character and Histogenesis of These Growths," by Jacob Furth; "Pathologic and Carcinogenic Effects of Plutonium," by H. Lisco and Miriam P. Finkel; "Studies on the Influence of Cosmic Radiation on Carcinogenesis," by F. H. J. Figge.

Isotopes—"Destruction of Rat Thyroid by Large Doses of Radioiodine I^{131}," by C. P. Leblond and D. Findlay; "The Collection of Radioactive Iodine by Benign and Malignant Tumors of the Thyroid," by R. W. Rawson, B. M. Dobyns, Ruth Hill and R. G. Fluharty; "The Effect of Radioactive Strontium on the Peripheral Blood Picture of the Normal Dog," by J. E. Nelson, J. G. Gibson, B. L. Vallee and M. A. Van Dilla; "Distribution of Zinc in Normal Blood and Organs Studies by Means of Zn^{65}," by B. L. Vallee, R. G. Fluharty and J. G. Gibson, 2nd; "The Metabolism in the Mouse of 1:2:5:6-Dibenzanthracene Labeled in the 9-Position with C^{14} (1)," by C. Heidelberger and H. B. Jones; "Factors Involved in Experimental Therapy of Metastatic Thyroid Cancer with Iodine-131," by T. B. Trunnell, A. F. Hooker and F. W. Foote; "The Therapy of Primary Polycythemia with Radioactive Phosphorus," by L. A. Erf; "Photographic Effect of Various Radiations on Special Dental Packets," by R. F. Cowing and C. K. Spalding; "Treatment of Diseases of the Hematopoietic System with Radiophosphorus," by B. E. Hall.

Radiation biology—"Carcinogenesis and Ultraviolet Irradiation," by H. P. Rusch; "The Effect of X-Irradiation on Tissue Rhodanase," by M. C. Bowman and W. R. Franks; "Effects of X-Ray Doses on the Controlled Greying Response in Mice," by H. B. Chase; "A Comparison of Radiosensitivity of Tumors Autogenous to Inbred Strains of Animals," by Anna Goldfeder; "The Effect of Radiation on the Biological Behavior of a Mouse Mammary Carcinoma," by H. S. Kaplan and E. D. Murphy; "The Behavior of the Tumor Cell Under the Influence of Irradiation and Chemicals," by P. C. Koller; "Excretion of Radium from the Mouse," by Joanne Weikel and Egon Lorenz; "Experimental Studies on the Influence of Radiation Quality, Dose Rate and Fractionating on the Direct Injury of Cells by Ionizing Radiations," by L. H. Gray.

FOURTH RADIOACTIVE SERIES ESTABLISHED

Two independent studies [*Physical Review* **72,** 3 (1947)] of the decay products of U^{233} have resulted in the establishment of a fourth radioactive series $(4n + 1)$. The name "neptunium" has been suggested for this radioactive decay family; thus, the family would receive its name from its longest

lived member in a manner similar to the naming of the uranium and thorium decay series.

The work on this project was done by an American group and a Canadian group. In the former, headed by G. T. Seaborg of the Radiation Laboratory, University of California, Berkeley, were F. Hagemann and L. D. Katzin of Argonne National Laboratory, Chicago, M. H. Studier of the Institute of Nuclear Studies, University of Chicago, and A. Ghiorso of the University of California Radiation Laboratory.

The Canadian group included A. C. English, T. E. Cranshaw, P. Demers, J. G. Harvey, E. P. Hincks, J. V. Jelley, and A. N. May. They worked at the Montreal Laboratory of the Division of Atomic Energy, National Research Council of Canada.

A number of the preceding members of the $(4n + 1)$ series have been reported previously as follows:

$$_{94}Pu^{241} \xrightarrow{\beta} {}_{95}Am^{241} \xrightarrow{\alpha} {}_{93}Np^{237} \xrightarrow{\alpha} {}_{91}Pa^{233} \xrightarrow{\beta} U^{233}$$

The remainder of the series is tabulated below.

Species	*Type of Radiation*	*Half-Life*	*Energy of Radiation (Mev)*
$_{92}U^{233}$	α	1.63×10^5y	4.83
$_{90}Th^{229}$	α	7×10^3y	4.85
$_{88}Ra^{225}$	β	14.8d	0.2
$_{89}Ac^{225}$	α	10.0d	5.80
$_{87}Fr^{221}$	α	4.8m	6.30
$_{85}At^{217}$	α	0.018s	7.00
$_{83}Bi^{213}$	α (2%), β (98%)	47m	6.0 (α), ~1.2 (β)
$_{84}Po^{213}$	α	3.2×10^{-6}s	8.30
$_{82}Pb^{209}$	β	3.3h	0.7
$_{83}Bi^{209}$	stable	—	—

RADIUM AND X-RAY SOCIETY CONVENES IN CHICAGO

The Seventh Annual Convention of the American Industrial Radium and X-ray Society will be held Oct. 22–24 at the Hotel Morrison in Chicago.

The following papers will be presented: "Profitable Mass X-ray Inspection," by Justin G. Schneeman; "Skin Thickness in Bronze Castings as Shown by X-ray of Thin Sections," by Carleton G. Lutts; "Polaroid Vectograph Technique Applied to Stereo-Microradiography," by Don M. McCutcheon and Merle F. Valade; "Development of a Universal Exposure Slide Rule for Radium Radiography," by Jay Bland and N. A. Kahn; "The Use of Isotopes in Industrial Radiography," by Gerald H. Tenney; "A Metallurgical Problem Solved by X-ray Diffraction," by Herbert Mermagen; "Coordinated Spectroscopy and X-ray Diffraction," by W. J. Poehlman and W. A. Kluck; and "Automatic Processing of X-ray Film," by F. Glenn Hamilton and Robert Sardeson.

Also "Influence of Field Size on Contrast and Exposure in Industrial Radiography," by E. Dale Trout and A. L. Pace; "Non-Destructive Testing in the Design, Manufacture, and Evaluation of Naval Ordnance," by Leslie W. Ball; "Application of Radiography in Die Casting," by E. W. Dively; "Electronic Applications to Non-Destructive Testing," by Arthur E. Johnson; "Deflected Beam Technique in Million-Volt Radiography," by Harold Wagner and Don W. McCutcheon; "The Application of the 20-Million-Volt Betatron to Industrial Radiography," by Jack T. Wilson; "Van de Graaff 2-Million-Volt X-ray Precision Radiographic Technique," by A. E. Burrill; and "The Use of Filters in Million-Volt Radiography," by G. M. Corney.

UNIVERSITY BUILDS CYCLOTRON SHIELD

A five-foot wall of concrete has been erected around the 4,000-ton cyclotron at the University of California as a result of experiments to determine the most effective shielding against the radiations created by the machine's new high-energy bombardments.

The research, conducted by Dr. B. J. Moyer who was assisted by Roger Hildebrand, Norman Knable, Dr. Thomas Parmley and Dr. Herbert York, was done under the auspices of the Atomic Energy Commission in

collaboration with the University's Radiation Laboratory.

Dr. Moyer, physicist of the Radiation Laboratory, has reported that, as the intensity of the beam produced by the cyclotron is increased, the thickness of concrete will be expanded to eight and eventually to ten feet.

He said that a number of elements were tested in addition to the concrete. Water, paraffin, graphite, aluminum and lead were all less effective than concrete. Copper was more effective, but would be impractical because of the expense.

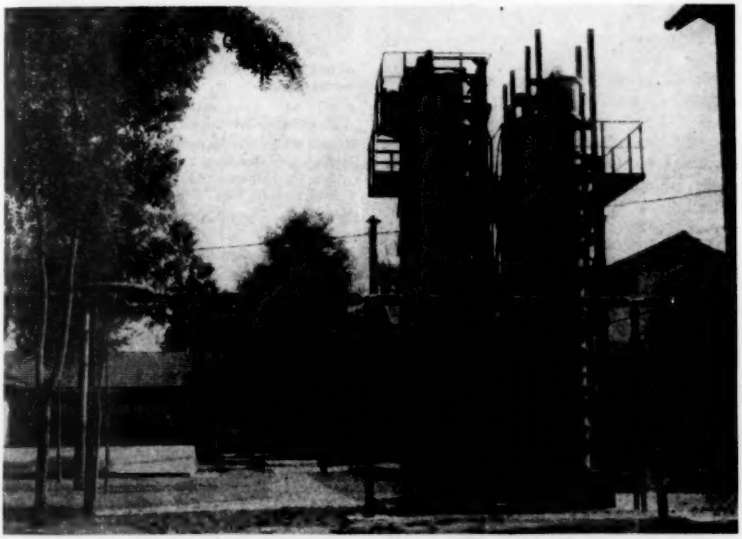
The concrete wall protects personnel primarily from the 100 Mev neutrons produced in 200 Mev deuteron and 400 Mev alpha particle bombardments by the cyclotron.

The five-foot wall cuts the intensity of the beam down to one hundredth its original strength. Dr. Moyer explained that this is sufficient protection at the present intensity of the beam. Even at present intensities, he said, the beam can be faintly detected when a Geiger counter is held behind the concrete at the point at which the beam is emerging from the cyclotron.

The experimental work was done with a concrete "igloo." Inside the "igloo" were placed detectors, and in front of the detectors were placed increasing thicknesses of concrete. The number of neutrons penetrating the concrete indicated the effectiveness of a given thickness.

Dr. Moyer found that a low atomic number and high density was the desirable combination of factors in cutting the beam. Under such circumstances the nuclear particles of a protective substance are crowded close together, increasing the frequency with which neutrons will be stopped.

The concrete blocks around the cyclotron weigh about 20 tons each. They are 5 ft wide, 5 ft thick, and 10 ft long.



France enters nuclear energy field—At Fort Chatillon and Le Bouchet powder works, both outside Paris, about 120 French technicians are working on an atomic pile in France's first step toward the practical application of nuclear energy. The pile is expected to reach full size in two years. Shown is an exterior view of the Le Bouchet works, which is specializing in turning out uranium.

RADIOLOGICAL SOCIETY MEETS

The 33rd annual meeting of the Radiological Society of North America will be held in Boston, Mass., at the Hotel Statler, Nov. 30 through Dec. 5. Refresher courses will be given, starting the afternoon of Nov. 30 and continuing every morning through Dec. 5. Details on the courses may be obtained from the chairman, Dr. Edgar V. Virden, 700 Professional Building, Kansas City, Mo.

NUCLEAR NEWSMAKERS

Dr. Howard J. Curtis, formerly director of biological research at Oak Ridge and Associate Professor of Physiology at Columbia University, is now chairman of the Physiology Department at Vanderbilt University Medical School, Nashville, Tenn.

Recently appointed to key positions in the Atomic Energy Commission were **Roger S. Warner, Jr.,** formerly coordinating engineer at Los Alamos Laboratory, as Director of Engineering; **John C. Franklin,** formerly vice-president of Trans-World Airline, as Manager of the Oak Ridge Office of Directed Operations; **Alfonso L. Tammaro,** formerly Assistant to the District Engineer, Manhattan District, as Acting Manager of Chicago Directed Operations; **Phillip S. Fogg,** president of Consolidated Engineering Corp., as Advisor to the Acting Manager of Chicago Directed Operations; and **Carleton Shugg,** general manager of Todd Shipyards in N. Y., as manager of the Hanford Directed Operations.

Rear Admiral John E. Gingrich, USN, Assistant Chief of Naval Operations, has been appointed Director of a newly-created Division of Security and Intelligence of the Atomic Energy Commission.

Six new assistant directors—**Dr. Frank C. Croxton, Dr. Clarence H. Lorig, Dr. Howard W. Russell, Ralph A. Sherman, Clarence E. Sims,** and **John D. Sullivan**—have been named by the Battelle Memorial Institute of Industrial and Scientific Research at Columbus, Ohio. The new appointees are all members of the Battelle staff.

Dr. Bruce S. Old has been appointed consultant to the Atomic Energy Commission, Division of Research, in the capacity of Chief Metallurgist. Dr. Old will continue his present work with Arthur D. Little, Inc., Cambridge, Mass., industrial research laboratory, and will serve the AEC on a part-time leave of absence.

Lauriston S. Taylor, chief of the X-ray Section of the National Bureau of Standards, has been elected an Associate Fellow in the American College of Radiology.

MEETINGS

Electrochemical Society — Fall Congress, Copley-Plaza Hotel, Boston, Mass., Oct. 15–18

National Metal Congress and Exposition—International Amphitheater, Chicago, Ill., Oct. 18–24

American Society for Metals—Chicago, Ill., Oct. 20–24

American Standards Association—Annual Meeting, New York, N. Y., Oct. 21–23

Pacific Chemical Exposition and Pacific Industrial Conference, sponsored by California section of American Chemical Society, Civic Auditorium, San Francisco, Cal., Oct. 21–25

Optical Society of America—Cincinnati, Ohio, Oct. 23–25

American Mathematical Society—New York, N. Y., Oct. 25

American Society of Clinical Pathologists—Annual Meeting, Drake Hotel, Chicago, Ill., Oct. 28–30

National Electronics Conference—Edgewater Beach Hotel, Chicago, Ill., Nov. 3–5

American Institute of Electrical Engineering—Midwest General Meeting, Chicago, Ill., Nov. 3–7

American Physical Society—Houston, Tex., Nov. 28–29

American Society of Mechanical Engineers—Annual Meeting, Atlantic City, N. J., Dec. 1–5

Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., Dec. 1–6

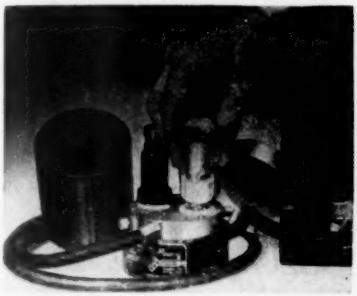
American Association for the Advancement of Science—Chicago, Ill., Dec. 26–31

American Physical Society—Chicago, Ill., Dec. 29–31

PRODUCTS and MATERIALS

BETA-RAY COUNTER

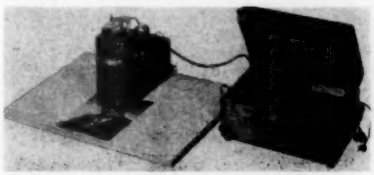
General Radio Co., 275 Massachusetts Ave., Cambridge 39, Mass. The type 1500-P2 Beta-Ray Counter has a window of 0.001-in. aluminum-alloy foil, which has a density of about 7 milligrams per sq cm. Illustrated is the preamplifier, with cover removed, to



show the counter and the arrangement for plugging counters in or out of the circuit. The counter shown has been designed to operate with GR's type 1500-A counting-rate meter.

TRANSMISSION DENSITOMETER

Photovolt Corp., 95 Madison Ave., New York 16, N. Y. The Electronic Transmission Densitometer has been used for checking the clouding of photographic negatives kept in places which are exposed to radiation and to check up on the integrated radiation at regular intervals. The instrument was actually designed for the measurement of the density of negatives in ordinary photography as well as in photolithography and photoengraving.



RADIATION DETECTOR

Victoreen Instrument Co., 5806 Hough Ave., Cleveland, Ohio. The Protexim-eter has been developed to measure scattered radiation accumulatively, the quantity being indicated visually on a calibrated meter scale. The scale is calibrated in milliroentgens with full-scale deflection 200 milliroentgens or

0.2 r. Midscale indicates 0.1 r which is the accepted standard for a daily tolerance dose.

INTERFERENCE FILTERS

Baird Associates, 33 University Rd., Cambridge 38, Mass. Interference filters have been designed for the solution of optical problems requiring narrow band transmission. It is claimed that a band width of 100–150 A.U. (half maximum transmission) can be obtained between 3,700 A.U. and 7,000 A.U. (tolerance ±50 A.U.). The fil-

ters, which are 2 in. square, have a "per cent transmission" of 20 to 35% of maximum, with a rapid falling off to approximately ½% minimum.

MIRRORS

Evaporated Metal Films Corp., Ithaca, N. Y. Three types of mirrors are available. Chroluminum is claimed to be opaque and to have a reflectivity that is above 85% throughout the visible and near ultraviolet spectrum. Duolux is a semi-transparent film and rhodium is an opaque film with a claimed reflectivity of above 70% throughout the spectrum.

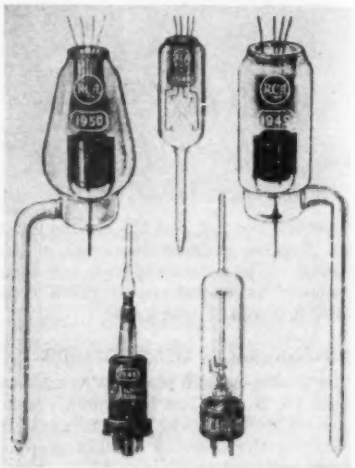
LEAD SHIELD

Radiation Counter Laboratories, Inc., 1451 E. 57th Street, Chicago 37, Ill. This type shield is claimed to be the accepted standard for shielding mica-window counters against cosmic and other types of radiation. It is fabricated from virgin lead 1½ in. thick and has a ⅛ in. inner lining of aluminum which absorbs the secondary radiation.

All slots through the lead are at angles to minimize entrance of any radiation. The door, hung from welded steel hinges, may be opened by finger action. A base switch turns on a replaceable standard lamp, facilitating the sample's being properly aligned on the tray of the mount. The latter has five reproducible geometries.

VACUUM GAGE TUBES

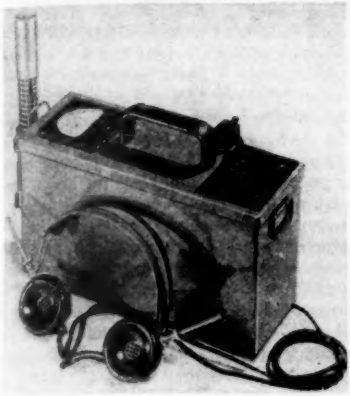
Radio Corp. of America, Camden, N. J. Type 1945 ionization gage tube is used in a new vacuum leak detector. Sensitive only to hydrogen, the tube is connected into a vacuum system and a jet of hydrogen is then played over the areas to be checked for leaks. A small amount of the gas increases ion current



in the tube to give an indication. Other ionization-type tubes are the type 1949 and type 1950. The 1946 is a thermocouple and the type 1947 is a Pirani gage.

PORTABLE COUNT RATE METER

Instrument Development Laboratories, 223 W. Erie St., Chicago, Ill. This portable beta-gamma count rate meter is 11 in. × 4 in. × 6 in. and weighs 9½ lbs. The Model 2610, with ranges of 0.2, 2 and 20 milliroentgens per hr



full scale, is battery-operated and uses two hearing-aid-type tubes in its count rate circuit. A visual reading of the amount of radiation present is given by a meter, and earphones are provided for an oral indication.

X-RAY SPECTROMETER

North American Philips Co., Inc., 100 E. 42d St., New York 17, N. Y. This Geiger-counter X-ray spectrometer is designed for use in the solution of industrial analysis problems. X-rays, directed upon a finely pulverized sample, are diffracted by the specimen.

The Geiger counter measures the diffracted rays, whose intensities and angular position are characteristic of the material, and with the aid of suitable electronic circuits, translates the impulses into a hill-and-valley curve on the chart.

RADIOCHEMICAL SERVICES

Tracerlab, Inc., 55 Oliver St., Boston 10, Mass. Eight chemical services, which facilitate the use of radioisotopes, are available through the Radiochemical Division. These services are: purification of isotopes, dilution and standardization of isotopes, storage of radioactive materials, isotope sharing plan, synthesis of radioactive compounds, radiochemical analyses, radiochemical research, and consultation on special problems.

Tracerlab is approved to receive isotope shipments from Oak Ridge as an agent for the purchaser. These isotopes may be obtained for the following uses, in order of priority: (a) publishable researches in the fundamental sciences, including human experimentation, which require relatively small samples; (b) therapeutic, diagnostic and tracer applications in human beings and publishable researches in the fundamental sciences which require larger samples; (c) training and education by accredited institutions in the techniques and applications of radioisotopes; (d) publishable researches in the applied sciences.

LABELED COMPOUNDS

Isotopes Branch, Field Operations, U.S. Atomic Energy Commission, P. O. Box E, Oak Ridge, Tenn. Carbon-14-labeled compounds are being made available as a result of research on synthesis procedures by the Clinton Laboratories. Methanol, in which 3% of the carbon atoms present are radioactive, is the first such compound to be prepared. It will contain 10 to 20 millicuries of C^{14} and will cost $100 per mc of C^{14} in the form of CH_3OH. Application for the labeled methanol should be made on Form 313, "Request for Radioisotopes."

ABSTRACTS

CHEMICAL PUBLICATIONS

An improved Geiger-counter arrangement for determination of radium content, F. Davis, *J. Research Nat. Bur. Standards,* **38,** 513–518 (1947). A Geiger-counter apparatus is described which consists of four counters in a square, with the source in the center. The counting rate for such an arrangement is approximately independent of the position of the sample. The only effect of the size and shape of the sample is the change in the percentage of absorption. A method of calculating the self-absorption of a sample is given.

The future of nuclear physics, E. Fermi, *J. Franklin Inst.* **244,** 1–3 (1947). An address by Fermi on the occasion of the award to him of the Franklin Medal.

The transport mean free path of thermal neutrons in heavy water, P. Auger, A. Munn, B. Pontecorvo, *Can. J. Research* **25A,** 143–156 (1947). The transport mean free path of thermal neutrons, l_t, was found to be 2.4 cm in pure heavy water. Heavy water (99.4 atoms of deuterium per 100 atoms of hydrogen) was placed between a cadmium plate and the top of a graphite pile, and a BF_3 counter interposed between the graphite and the cadmium. The latter could be moved up and down by means of a micrometer screw. The source of neutrons was 2.4 g of radium mixed with beryllium. The neutron density in the heavy water was measured at various distances from the cadmium plate, and was found to be a linear function of the distance, d. When a plot of density versus distance is extrapolated, the density vanishes at $d = 1.64$ cm behind the plate. Since $d = 0.71 l_t$ from transport theory, l_t may be calculated.

Portable Geiger-Müller counters, W. Hushley, K. Feldman, *Can. J. Research* **25F,** 226–35 (1947). Details of circuit design and application are given for three models of portable Geiger-Müller counters of light weight and low power consumption. These counters, which are suitable for field use as detectors of radioactive minerals, all use selfquenching G-M counter tubes operated at about 1000 v. The high-voltage circuit consists essentially of a multivibrator with an inductive load in the plate circuit of one tube, and a rectifier through which the pulses induced in the inductance charge a capacitor. A negative pulse from the G-M tube is fed to a trigger circuit which actuates headphones. In two of the models each pulse from the G-M tube produces a single oscillation of the trigger circuit, while in the third model a neon tube discharge circuit is used to give one headphone pulse for every ten from the G-M tube, and a counter is provided. The scaling factor in the latter circuit may be altered by changing circuit constants. The weights of the counters described are 1, 6, and 11 lb. respectively.

The diffusion length of thermal neutrons in heavy water, B. Sargent, D. Booker, P. Cavanagh, H. Hereward, N. Niemi, *Can. J. Research* **25A,** 134–142 (1947). The diffusion length of thermal neutrons in heavy water, which is one of the nuclear physical properties required in the design of chain-reacting piles that contain this moderator, was directly measured. A continuous flux of thermal neutrons, obtained from a block of beryllium at the end of the tube of an X-ray generator, was passed into a large cylindrical tank of heavy water located on a graphite column containing the source of photoneutrons. Small indium detectors were used to determine the neutron density in the tank at selected points along two diameters at right angles in each of three horizontal planes, and at 10-cm intervals along the axis of the tank. The transverse measurements were fitted to a Fourier-Bessel series in which the amplitudes of the harmonics were relatively small. Corrections were made for the absorption of neutrons in the axial detector tube, enclosed framework

and indium detectors, and in the light hydrogen in the heavy water. The diffusion length of thermal neutrons in 100% D_2O is 171 ± 20 cm, and the capture cross section is (0.92 ± 0.22) × 10^{-27} cm^2 per molecule of D_2O for neutrons of velocity 2200 meters per second.

Tolerance concentrations of radioactive substances, K. Morgan, *J. Phys. & Colloid Chem.* **51,** 984–1003 (1947). The tolerance dose limits for a 24-hour exposure are 100 milliroentgen (mr) for x- and γ-radiation, 100 milliroentgen-equivalent-physical (mrep) for β-radiation, 10 mrep for α-radiation, 20 mrep for fast neutrons and protons, and probably 5 mrep for thermal neutrons. The factor of safety for these limits is probably not more than 2 or 3. Methods are given for calculating tolerances for various types of radioactive elements introduced into the body under different conditions. It is assumed that the only harmful biological effects of radiation are produced by the resulting ionization, or that the harmful results are proportional to the amount and distribution of ionization. A table is given showing the tolerance concentrations for different body intakes of various important radioactive elements.

Spatial distribution of neutrons in hydrogenous media containing bismuth, lead, and iron, A. Munn, B. Pontecorvo, *Can. J. Research* **25A,** 157–167 (1947). The spatial distribution of thermal neutrons (measured by dysprosium detectors) and of resonance neutrons (measured by indium detectors protected by cadmium) were investigated in various heterogeneous water-heavy element media. Two different neutron sources, Ra-α-Be and Ra-γ-Be, were used to provide neutrons of different energy. The source was fixed in a tank filled with the heterogeneous medium, and the detectors were irradiated at various distances, r, from the center of the source, measured in several directions. The spatial distributions for various conditions are plotted and summarized in tables. The mean square distance from the source, $(r^2)_{av}$, is least for a mixture of water and iron. The latter, out of all the media studied, is the most efficient shield for neutron generating machines such as piles and cyclotrons.

Some properties of the radiation from radiomanganese-54 and the adsorption of manganous manganese on hydrous ferric oxide, D. Anderson, *J. Phys. & Colloid Chem.* **51,** 956–962 (1947). Radiomanganese-54 and nonradioactive manganese were used to study the adsorption of manganous manganese by hydrous ferric oxide. For ratios of 10 mg of iron to 0.03 mg of manganese and 10 mg of iron to 5 mg of manganese, less than 12% of the manganese is precipitated at a pH of 4 in the presence of ammonium nitrate. The percentage of manganese adsorbed increases with pH to a maximum of 100% at a pH of 8. Ammonium salts interfere with the adsorption of the manganese, but this is not due to a buffer effect that changes the pH of the system. The effect of hydrous ferric oxide, manganese dioxide, cellophane, aluminum, and lead on the radiation from $_{25}Mn^{54}$ was studied using a Lauritsen quartz-fiber electroscope.

Cross sections for production of artificial mesons, C. Morette, H. Peng, *Nature* **160,** 59–60 (1947). The theory of radiation damping was used to compute the cross sections for the production of mesons in two collision processes: nucleon + nucleon → meson + nucleon + nucleon, and γ-ray + nucleon → meson + nucleon. Tables are given for the cross sections found for each process for various energies of incident nucleon and γ-rays. Meson production by γ-rays is comparable with that by nucleon-nucleon collisions in the energy region $2.5 - 3.5 \times 10^8$ ev.; at lower energies, the production of mesons by γ-rays is more effective, at higher energies that by nucleon-nucleon collisions.

Slow cosmic ray mesons at sea-level, G. Evans, T. Griffiths, *Nature* **159,** 879–881 (1947). Ilford C2 emulsions of 40μ thickness were exposed at sea level. In 3 cm^2 of emulsion which were ex-

amined, 15 long tracks due probably to protons of energy 10–20 Mev, a track of length 180μ which appears to be that of a slow meson coming to rest in the emulsion, together with a star of 11 charged particles, have been found. The scattering along the meson track together with grain count measurements indicate that the mass of the meson was $250 \pm 50m_e$. The star may be another example of meson capture by a nucleus. Photographs of the tracks are given.

The trans-uranium elements, G. Seaborg, E. Segrè, *Nature* **159,** 863–865 (1947). A review of the discovery of the trans-uranium elements with 19 references.

The meson spectrum near sea-level, M. Corte, T. Fazzini, S. Franchetti, *Nature* **159,** 845 (1947). The value of γ in the production spectrum of mesons $dN = \text{const. } p^{-\gamma}dp$ was redetermined by a method which takes into account the variable energy-loss of mesons through the atmosphere. The basis of the computation is Rose's formula for the vertical meson spectrum at sea-level, with the hypothesis of an initial $p^{-\gamma}$ spectrum instead of $\epsilon^{-\gamma}$ (where p and ϵ are the meson energy and momentum, respectively). The value of γ was found to be 3.20, confirming that γ has a value somewhat higher than usually accepted.

Nuclear thermodynamics and showers, B. Agarwala, K. Singwi, *Nature* **159,** 816 (1947). The study of dense, high temperature (where $kT \sim mc^2$, m being the mass of the electron) thermodynamic assemblies consisting of atomic nuclei, nucleons, electrons and positrons may throw light on the "explosion" showers associated with cosmic rays. On the basis of these ideas, the relative probabilities for the emission of light nuclei from a highly excited heavy nucleus may be estimated. Further, estimates may be made of the number of mesons and electrons (positive and negative) in an excited nucleus. The results of several such calculations are given.

Correcting for the absorption of weak beta-particles in thick samples, P. Yankwich, T. Norris, J. Huston, *Ind. Eng. Chem., Anal. Ed.* **19,** 439–441 (1947). When isotopes such as C^{14}, S^{35} and $As^{72,73}$, which decay by the emission of beta-particles of low energy, are used in tracer work, errors are introduced due to the absorption of the radiations in the material of the sample itself. In this paper is given a general experimental method for obtaining curves for correcting for self-absorption in the sample material, with data for $BaC^{14}O_3$ as an illustration. A function, $G(X)$, is defined as the observed activity at a layer thickness X divided by the activity of an infinitely thick layer. A plot of $G(X)$ versus sample thickness, X, in mg/cm² may be made from experimental measurements. Using this curve the observed activity for any particular value of X may be converted to the activity of an infinitely thick layer. Another function, $J(X)$, is defined as the observable fraction of the true maximum specific activity (specific activity of an infinitely thin layer), and may be calculated for any value of X from the $G(X)$ versus X curve. The actual activity or specific activity of a sample of thickness X may be obtained from a plot of $J(X)$ versus X. Errors, due to obliquity of the paths of emitted beta particles, of less than 2% were found with counters having geometric efficiencies varying from 7.6 to 20.5%.

. . . I. W. RUDERMAN

LIFE SCIENCE PUBLICATIONS

Use of radioactive hydrogen for measurement *in vivo* of total body water, N. Pace, L. Kline, H. Schachman, M. Harfenist, *J. Biol. Chem.*, **168,** 459 (1947). Water containing tritium (HTO) was prepared from beryllium targets which had been subjected to deuteron bombardment, the reaction being $Be^9 + D^2 \rightarrow Be^8 + H^3$. The targets were dissolved in HCl, the gaseous tritium formed converted to water by being passed over copper oxide and then

collected in a liquid air trap. Stock solutions of tagged water were injected intravenously into two male rabbits and into a human. Blood samples were withdrawn at intervals and the tritium activity measured by admitting the radioactive water vapor at up to 2 mm Hg into a Geiger-Müller counter tube.

Total body water of the rabbits was obtained from the activities of the stock solution and body water and the known volume of stock solution injected. Total body water was also estimated on the basis of a constant fraction, 73.2% of the lean body mass, after measurement of total body fat by the body specific gravity method. A third method of estimation, that of weight change during desiccation, was also used. The three methods yielded an average value of 54% to 55% with fairly good agreement. There was also close agreement in the determination of human body water between the body specific gravity and the tritium oxide dilution methods with an average value of about 65%, which is in accord with accepted previous values.

Less than 30 minutes were needed for equilibrium to be reached in the body water of the rabbit and about an hour for the human, which is believed to indicate a relationship between body size and time of equilibration. A source of error was the uncertainty of measurements of activities in the range of the background value. The accuracy of the method is believed to be as good as the method using deuterium oxide.

The effect of succinic acid dehydrogenase on deuterium-labeled succinic acid in the absence of hydrogen acceptors, E. Weinman, M. Morehouse, R. Winzler, *J. Biol. Chem.* **168, 717** (1947). Deuterosuccinic acid was prepared and incubated anaerobically with succinic acid dehydrogenase prepared from rabbit kidneys. Methylene blue was included in some of the incubations. The mixtures were allowed to react at pH 7 from 4 to 31 hours. The succinic acid was then isolated and the deuterium content determined. A little exchange of hydrogen atoms of the medium water with the deuterium atoms of the deuterosuccinic acid in the absence of enzyme was found in the control experiments. A significant increase in exchange was noted, however, where the enzyme preparation was used. The presence of methylene blue which acted as a hydrogen acceptor had no effect on the rate of exchange.

Rate of hydrogen exchange was compared to rate of dehydrogenation. Activity of the enzyme, its concentration, and length of incubation were known; these three multiplied together gave a certain percentage of succinic acid that would have been oxidized had a suitable acceptor been present. It was found that this percentage was roughly comparable to the deuterium-hydrogen exchange percentage. The authors suggest, therefore, that the same enzyme, succinic acid dehydrogenase, catalyzes the α- and α'-hydrogen exchange as well as the dehydrogenation of succinic acid to form fumaric acid.

Intravaginal radiation therapy, J. Bouslog, *Am. J. Roent. Rad. Therapy* **57,** 665 (1947). Because of anatomical variations of the cervix and uterus, there is no standard method of treatment using radium applications from the vaginal surface. Spreading of cancer of the cervix is discussed. It is concluded that it is best arrested by applying uniform irradiation to all the cancer cells in the pelvis. The importance of uniform irradiation and the difficulties in obtaining it are elaborated. To concentrate roentgen radiation upon a particular organ, it is necessary to know the depth of the lesion and the position of the lesion as projected upon the surface of the body in relation to certain fixed points. The necessary technique to deliver the lethal dose is then determined.

Data concerning the type of machine used in intravaginal therapy, the distances involved and the necessary filters are given. The reactions from intravaginal therapy are the same as those from external applications. Occasionally, delayed reactions such as ulceration and increased discharge occurred when over 5000 r were delivered to the site of the cancer. In the

author's experience the technique has given better results than the use of radium or external irradiation alone. The method cannot be used in vaginismus, vaginal atresia and narrowness of the vagina in unmarried women since introduction of the radiation cone is not possible.

Anomalous distribution of antimony in white rats following the administration of tartar emetic, A. Ness, F. Brady, D. Cowie, A. Lawton, *J. Pharmacol. Exptl. Therap.* **90,** 174 (1947). A study was made of the distribution of antimony in the tissues of white rats and dogs following parenteral administration. Radioantimony was prepared by the bombardment of a copper alloy of antimony as a probe target in a cyclotron. Two isotopes of antimony were used, Sb^{124} with a half-life of 60 days and Sb^{122} with a half-life of 2.8 days. The radioantimony was converted to tartar emetic which was then injected intravenously into dogs and white rats.

In dogs the antimony level in the blood dropped rapidly during the first eight hours and only small amounts remained after this time. In white rats, the antimony level in the blood paralleled those of dogs for the first four hours. However, after that the antimony level rose rapidly and at 72 hours it was 20 times as large as it was at four hours. The rate of disappearance of antimony from dog blood is almost identical with that observed in humans. The livers of dogs showed a higher concentration of Sb two and three days after the injection than did those of white rats even though the dogs had received smaller doses. The spleen concentrations appeared similar. Rat kidneys showed considerably more Sb than did dog kidneys at the same intervals.

No clue is given to the chemical state of the antimony which is determined quantitatively by its radioactivity. There is some indication that the Sb compound appearing in the blood of the white rat at later intervals is considerably less toxic to the rat than its tartar emetic precursor. The authors suggest that the results obtained in screening antimonial compounds in white rats be interpreted with caution until more is learned of the phenomenon.

The distribution, retention, and excretion of radiophosphorus following thyroparathyroidectomy, or bilateral nephrectomy, and the administration of parathyroid extract, W. Tweedy, M. Chilcote, M. Patras, *J. Biol. Chem.* **168,** 597 (1947). A study was made of the disposition of radioactive phosphorus administered to untreated rats which had been thyroparathyroidectomized, untreated bilaterally nephrectomized rats and also to rats similarly operated on and injected with parathyroid extract. Fecal and urinary excretion of radioactive phosphorus fell markedly in the first 24-hour period after the thyroparathyroidectomy. The retention of administered radiophosphorus in the various tissues appeared to depend upon their relative mass and phosphorus content.

The urinary and fecal excretion of radiophosphorus increased greatly 48 hours after thyroparathyroidectomy and in 15 to 26 days exceeded the control value. The retention of radiophosphorus decreased as its excretion increased but only in the case of muscle tissue did the retention drop below the control value. With the injection of parathyroid extract a reversal of the retention of radiophosphorus in the tissues during the first 24 hours after thyroparathyroidectomy and increased urinary excretion of radiophosphorus occurred. The effect of increasing urinary excretion of radiophosphorus by the parathyroid extract is viewed as evidence of direct action of the parathyroid hormone upon the kidney. No effect upon the disposition of radiophosphorus by parathyroid extract administration was observed after bilateral nephrectomy.

Cosmic radiocarbon and natural radioactivity of living matter, A. Grosse, W. Libby, *Science* **106,** 88 (1947). The effects on the human body of radiocarbon produced by cosmic radiation are compared with radium and potas-

sium. The basis of comparison is the number of disintegrating atoms (or rays) per human being per unit time. This is included in a table which shows also the per cent weight of the constituents in the body, the total weight of the constituents, and the specific activity of the constituents. The number of particles penetrating the body from cosmic radiation ranges from 1500 to 7500 depending on whether the human being is in a standing or lying position. From a comparison of the data it is seen that cosmic radiocarbon is below potassium but far above radium and other natural elements in total activity.

Efficient deep tumor irradiation with roentgen rays of several million volts, J. Trump, C. Moster, R. Cloud, *Am. J. Roent. Rad. Therapy* **57,** 703 (1947). The characteristics of roentgen rays produced by constant potential of from one to four million volts with special emphasis on two million volt radiation are discussed. The "sub-cutaneous effect" of high-energy roentgen rays which results in low skin dose is described along with the technique of beam aperture, treatment distance, and cross-fire which makes possible deep tumor doses much higher than those sustained by skin or even tumor adjacent tissue. High-energy roentgen rays increase the efficiency of deep tumor treatment even without cross-fire. Cross-fire becomes more effective with penetrating, low scattering, skin favoring roentgen rays of several million volts' energy. For a given deep tumor dose, a smaller total dose is absorbed by the patient when high-energy roentgen rays are used than when 200 kv roentgen rays are used. As the roentgen-ray voltage increases above several million, disadvantageous characteristics, such as non-uniformity of intensity across the beam and high exit dose, occur.

The metabolic interrelations of thyroxine and diiodotyrosine in the thyroid gland as shown by a study of their specific activity-time relations in rats injected with radioactive iodine, A. Taurog, I. Chaikoff, *J. Biol. Chem.* **169,** 49 (1947). To determine whether diiodotyrosine is a precursor of thyroxine, rats received, by way of the tail vein, an isotonic solution of radioactive iodine without normal iodine as a carrier and were sacrificed over intervals of 15 min to 50 hr. The thyroid glands were homogenized, the proteins precipitated and hydrolyzed and separated into diiodotyrosine and thyroxine fractions. The supernatants of the protein precipitations were combined for determination of non-protein-bound iodine. The amount of iodine and the radioactivity in each fraction were then determined.

The distribution of normal iodine between the thyroxine and diiodotyrosine fractions was very constant among different animals. The distribution of radioactive iodine in the (organic and inorganic) fractions was also fairly constant at each interval. As early as 15 min after the injection, 95% of the radioactive iodine appeared in the organic fraction. Over 80% was in the diiodotyrosine fraction and 10 to 15% in the thyroxine fraction. At all the intervals noted, the fraction of radioactive iodine precipitated with trichloracetic acid, that is, the iodine in the protein or organic portion, was over 95%. The relative amount in the thyroxine fraction increased steadily reaching 25% at the end of 50 hr.

Specific activities of the iodine of the suspected precursor, diiodotyrosine, and thyroxine were plotted against time, using the average values of several animals. The graphs obeyed the criteria set up by Zilversmit *et al.* for determining if a substance is a precursor of another. Using these graphs it was determined that the turnover time of thyroxine is about 24 hr. The rate of thyroxine secretion, as calculated by a method of Zilversmit, is approximately 1.5 gamma per 100 gm of body weight per 24 hr. This is at variance with results obtained by others whose determinations were based on different principles.

The uptake of radioactive phosphorus by the calcified tissues of normal and choline-deficient rats, W. Neuman, R. Riley, *J. Biol. Chem.* **168,** 545 (1947).

A group of rats of both sexes were placed on a synthetic diet which was choline deficient and contained guanidoacetic acid. [Another group was placed on an adequate synthetic diet.] After three days, both groups received intraperitoneal injections of inorganic phosphate containing radioactive phosphorus. The animals were then sacrificed at intervals ranging from ½ to 16 hr. The femurs were extracted with alcohol, ashed and dried, dissolved in HCl and analyzed for phosphate and radioactivity using Bale immersion-type scale-of-four Geiger-Müller counters.

It was found that the inorganic blood radiophosphate fell rapidly just after injection and was leveling off at 16 hr while the bone radiophosphate rose rapidly and maintained a relatively high value for all the intervals observed. Rapid accumulation of tracer in the bone was attributed to other effects besides normal growth. Results obtained were deemed inconclusive. A study was made of the calcification of the bones of the choline deficient rats and it was concluded that choline deficiency has no effect. A possible mechanism for the rapid accumulation of radioactive phosphorus in the bone was discussed. It was concluded that this unexpected uptake, not connected with growth, seriously decreased the value of tagged phosphate in bone studies.

Intermediates in the biological oxidation of isotopic acetoacetate, J. Buchanan, W. Sakami, S. Gurin, D. Wilson, *J. Biol. Chem.* **169,** 403 (1947). Phosphate extracts of rabbit kidney were prepared capable of oxidizing acetoacetate with the addition of other accessory substances and to a much lesser extent acetate. This difference in the rates of metabolism of acetate and acetoacetate is seen as partial evidence that acetate is not an intermediate in the oxidation of the latter. However, it is not known conclusively that, in this extract, acetate and acetoacetate metabolisms may be accounted for exclusively by the tricarboxylic acid cycle. The oxidative rate of acetoacetate was considerably increased by the addition of alpha-ketoglutarate but its action was not believed to be of a catalytic nature. It was found that citrate is also readily oxidized by the kidney extract.

Isotopic acetoacetate was incubated anaerobically with non-isotopic acetate and alpha-ketoglutarate and the acetate isolated at the end of the experiment contained much less C^{13} than did the alpha-ketoglutarate. The authors concluded that acetate is not a direct intermediate in the oxidative utilization of acetoacetate via the tricarboxylic acid cycle.

A synthesis of methionine containing radiocarbon in the methyl group, D. Melville, J. Rachele, E. Keller, *J. Biol. Chem.* **169,** 419 (1947). A synthesis of L-methionine containing radiocarbon (C^{14}) in the methyl group starting with radioactive barium carbonate is described. Radioactive barium carbonate is first converted to the bicarbonate which is then reduced in the presence of catalytic palladium black to form potassium formate. The potassium formate is then esterified with methyl sulfate. The methyl formate thus formed is reduced catalytically to methanol using copper chromite. The radioactive methanol is converted to methyl iodide on treatment with hydriodic acid. Methyl iodide is condensed with the sodium derivative of homocysteine in liquid ammonia to yield the desired compound. Pictures of the semi-micro apparatus used at various stages are included.

Distribution of labeled carbon in sugar from barley, S. Aronoff, H. Baker, M. Calvin, *J. Biol. Chem.* **169,** 459 (1947). Radioactive sugars were prepared from barley seedlings which had assimilated $C^{14}O_2$. In order to determine the distribution of radiocarbon among the various carbons, the sugar was degraded by fermentation with yeast and Lactobacillus casei. The sugars were prepared from two types of barley seedlings, one with roots and one without. Because of the methods employed it was not possible to distinguish between

carbon pairs 1–6, 2–5 and 3–4. The tabulated results show that the 3–4 carbon pair had the highest isotope concentration, followed by the 2–5 carbon pair, with the 1–6 carbons having the least isotope. If the hexoses are formed from triose phosphates, it is seen that the greatest activity is in the terminal carbons which eventually become carbons 3 and 4 of the hexose.

A symposium: radiation necrosis, A. McIndoe, R. Forbes, B. Windeyer, *Brit. J. Radiol.* **20,** 269 (1947). Incorrect uses of radiation treatment are discussed along with the difficulties of determining correct dosages in some cases. To cut down the number of cases where radiation necrosis occurs it is suggested that radiation therapy be strongly controlled in benign cases where other methods of treatment are available. Varying degrees of radiation necrosis are sometimes unavoidable and their extent will depend upon individual idiosyncrasies and the skill of the operator. The obligations and scope of service of the radiologist are set forth. A definition of reasonable skill is given along with a presentation of new forms of treatment. The last speaker goes into detail concerning radiation necrosis of various areas, causes and characteristics.

Radiation doses received by the skin of a patient during routine diagnostic X-ray examinations, J. Martin, *Brit. J. Radiol.* **20,** 279 (1947). It was found that appreciable doses were received during X-ray diagnosis. Greatest care was found to be necessary in dental and pregnancy radiography. In almost all cases doses could be cut in half by increasing skin focal distance or filter or both. A table is given covering a number of the parts of the body showing the range of dose to be expected during an X-ray examination.

A study of the mechanism of fatty acid oxidation with isotopic acetoacetate, J. Buchanan, W. Sakami, S. Gurin, *J. Biol. Chem.* **169,** 411 (1947). A study was made of the metabolism in liver tissues of ketone bodies and fatty acids using octanoic acid labeled in the carboxyl group and acetoacetate labeled either in the carboxyl or carbonyl position. Acetoacetate did not split to any appreciable extent into two carbon fragments which could then recondense at random to form acetoacetate. When acetoacetate labeled in the carbonyl position was incubated in liver tissue, the isolated acetoacetate contained very small amounts of C^{13} in the carboxyl position, and vice versa.

Where isotopic octanoic acid was oxidized to form acetoacetate, the results were different from those of previous investigators. Instead of equal amounts of isotope in the carbonyl and carboxyl groups, it was found that the ratio was 0.9 to 0.6 with the carboxyl position containing the higher concentration.

The authors conclude from the experiments that the appearance of isotope in the carbonyl carbon of acetoacetate during the metabolism of carboxyl isotopic octanoate in liver slices does not result from a preliminary formation of isotopic acetoacetate followed by a splitting of the acetoacetate into two carbon fragments which recondense at random to reform acetoacetate labeled in both the carboxyl and carbonyl positions.

Production of increased capillary fragility in rats following irradiation, J. Griffith, Jr., E. Anthony, E. Pendergrass, R. Perryman, *Proc. Soc. Exp. Biol. Med.* **64,** 331 (1947). A method for measuring capillary fragility in rats was developed. Under general anaesthesia the peritoneal cavity is opened, the abdominal wall is carefully folded back until an artery and vein are disclosed. Then the peritoneum is grasped on each side of the vessels and stretched between the fingers so that the lumen of the vein is obliterated. Tension is maintained for two minutes and then relaxed. In a positive case a number of hemorrhages will occur but none in the normal case. Radon ointment was injected into the peritoneal cavity of normal rats and fragility was tested for one to eight weeks afterwards. In every animal, fragility was markedly increased.

Effect of rutin on recovery time from radiation injury in rats, J. Griffith, E. Anthony, E. Pendergrass, R. Perryman, *Proc. Soc. Exp. Biol. Med.* **64,** 332 (1947). Rats were given radiation to one leg. Half of them were given a small quantity of rutin, a flavonol derived from a number of plants, which was implanted along the lateral aspect of the abdominal wall. These doses were repeated every third day for 36 days. The observed reaction consisted of an erythema, a moderate swelling and ulceration in some cases. It appeared that rutin hastened the recovery time after irradiation.

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PHYSICAL PUBLICATIONS

Carbon dioxide filled Geiger-Müller counters, S. Brown, W. Miller, *Rev. Sci. Instr.*, **18,** 496–500 (1947). A detection method for measuring C^{14} uses the activity as a constituent of the CO_2 filling in a Geiger-Müller counter. Carbon dioxide offers special problems in counter discharge. Negative ion formation at the cathode is prevented by mixing in a gas of lower ionization potential than CO_2, thus preventing the CO_2 ions from reaching the cathode. The counter is not selfquenching; a quenching circuit is used.

Internal cyclotron fargets, A. F. Reid, *Rev. Sci. Instr.*, **18,** 501–503 (1947). Maximum efficiency in the production of radioelements by bombardment of a target is an important feature. The following requirements are discussed: (a) rapid heat transfer to the cooling system; (b) high melting point, low vapor pressure, negligible decomposition and firm binding to the probe; (c) as large a fraction as possible of bombarding nuclei available for the desired reaction. The optimum thickness of target depends on the deuteron and reaction energies and the stopping power and molecular weight of target material. Some general rules are given for good binding of the target material to the copper on which it is often plated. A formula is derived for the efficiency of various target materials and some experimental results given.

On the time required for the fission process, R. Wilson, *Phys. Rev.*, **72,** 98–100 (1947). The technique employed is to determine how far the recoiling U^{238} nuclei (formed from the absorption of fast neutrons in U^{238}) travel before fission occurs. Two ionization chambers are used as detectors. Results show less than 5×10^{-8} of fissions were delayed by as much as 10^{-8} sec.

Results of H^3 bombardment of Ag, leading to Pd^{109}, D. Kundu, M. Pool, *Phys. Rev.*, **72,** 101–108 (1947). H^3 was produced by Be (d, H^3) and Ag (d, H^3) reactions and the H^3 particles, at an energy of about 10 Mev, allowed to impinge on Ag foils. The 13-hour Pd^{109} activity was produced in the silver by the reaction Ag^{109} (H^3, He^3) Pd^{109}, and the reaction threshold estimated at 1.1–1.5 Mev. Decay curves are given and various other reactions ruled out. Ranges of H^3 particles in various materials are discussed.

A bent-crystal neutron spectrometer and its application to neutron cross-section measurements, R. Sawyer, E. Wollan, S. Bernstein, K. Peterson, *Phys. Rev.*, **72,** 109–115 (1947). With the use of the chain-reacting pile, sufficiently intense slow neutron beams are available to make possible measurements using crystal spectrometers. To permit greater intensity and resolving power at small angles (corresponding to neutron energies greater than 1 ev), a transmission-type bent-crystal spectrometer was used. Its focusing properties were good for smaller angles. Measurements were made with neutron beams of energy from 0.005 ev to 2.0 ev. The 0.178-ev resonance in Cd was investigated, as was the resonance in Ir. Breit-Wigner constants were obtained for both of these resonances.

Measurements of the slow meson intensity at several altitudes, B. Rossi, M. Sands, R. Sard, *Phys. Rev.*, **72,** 120–125 (1947). The characteristic decay time of mesons was used to detect them

separately from other more abundant components of cosmic radiation. Delayed coincidences among two counters in front of the absorber and two behind it are produced by mesons which decay in the absorber, giving off electrons. The number of these coincidences is plotted against delay time for various altitudes. Absolute measurements are difficult to obtain because the detection probability of decay electrons is not accurately known, but relative intensities are given for various altitudes.

The transition effect for large bursts of cosmic-ray ionization-II, C. Montgomery, D. Montgomery, *Phys. Rev.*, **72,** 131–134 (1947). The bursts of cosmic-ray ionization in a chamber covered with thin plates of various materials were measured. Two agencies operate to produce ionization bursts: (a) cascade showers from the atmosphere multiplied in the shield (this effect predominates for bursts of larger size), and (b) smaller bursts, not multiplied by the shield, and seemingly produced by nuclear disintegrations ("stars"). These two effects are separated by analysis of the data; from the number of air showers, the energy spectrum of cosmic radiation at very high energy is calculated and found to be proportional to $E^{-3.1}$ near 2×10^{15} ev.

Directional properties of fission neutrons, R. Wilson, *Phys. Rev.*, **72,** 189–192 (1947). By using a rotating collimating system, it was possible to measure the number of neutrons emitted at various angles to the direction of fission fragments. Results are consistent with the theory of isotropic evaporation of neutrons from moving fission fragments.

A thermal neutron velocity selector and its application to the measurement of the cross section of boron, E. Fermi, J. Marshall, L. Marshall, *Phys. Rev.*, **72,** 193–196 (1947). A mechanical velocity selector with rotating shutter and multiple sandwich of cadmium and aluminum sheets is described. It is useful for neutron energies below 3 ev. The cross section of BF_3 at several pressures was measured for neutrons of various velocities. The relation of the average velocity of pile neutrons to the thermal agitation velocity was also investigated.

Scattering of fast neutrons by helium, T. Hall, P. Koontz, *Phys. Rev.*, **72,** 196–202 (1947). Study was made of angular distribution of helium recoils for neutrons of energy 0.6–1.6 Mev, obtained from Li (p,n) reaction with protons from a Van de Graaff generator. Pulse height gave recoil energy, which gave the angle of scattering. This also allowed an estimate of total cross section, which agreed with one of the two contradictory sets of measurements previously made.

Distributions of neutrons in the atmosphere, H. Agnew, W. Bright, D. Froman, *Phys. Rev.*, **72,** 203–206 (1947). Measurements were made to an altitude of 36,000 feet in B-29s using BF_3 counters enriched in B^{10}. The spectral distribution was roughly investigated by placing various shields around the counters (cadmium, boron, paraffin, and bare).

Collision cross sections of carbon and hydrogen for fast neutrons, W. Sleator, *Phys. Rev.*, **72,** 207–219, (1947). Collision cross sections of carbon and hydrogen for neutrons of energy 6–22 Mev. The neutron sources were the (d,n) reactions of Li and Be, deuterons being obtained from a cyclotron. The detector was a paraffin-faced ionization chamber. A differential method allowed the measurements to be made on an energy interval of almost arbitrary size at any energy. The experimental constrictions and corrections in computation are described in detail, and results compared with measurements of previous investigators. The n-p cross section is compared with the various results given by various interactions.

On selfquenching halogen counters, R. Present, *Phys. Rev.*, **72,** 243–244 (1947). The selfquenching counter can operate as it does because of the absence of secondary-election emission when the positive ion sheath reaches the cathode

and is neutralized. The predissociation of molecules of a polyatomic gas in 10^{-13} sec, before they can make an inelastic collision with the wall, makes secondary-election emission negligible. The spectra of various halogen Cl_2, Br_2 gases are interpreted as making counters of Cl_2, Br_2 selfquenching. A carbon cathode in an I_2 counter should prevent secondary emission. Time lag in the initiation of discharge makes halogen counters unsuitable for coincidence experiments in which the efficiency must be high and the resolving time low.

The scattering of 4.2 Mev protons by protons, A. May, C. Powell, *Proc. Roy. Soc.*, **190A,** 170–180 (1947). The method used to detect the scattered particles is a photographic one, consisting of a large number of photographic plates adjusted radially about a scattering foil, each plate recording particles scattered at a single angle with respect to the primary beam, which was obtained from a cyclotron. The angular resolving power is of the order of 2°, and the different groups of scattered and disintegration particles are easily distinguishable through range measurements in most cases.

Various scatterers were used (hydrogen, acetylene, methyl iodide) along with various pressures and exposure times. The angular distribution of the scattered particles is found to be isotropic in the center of gravity system from 50° to 140°. The theory of elastic scattering is outlined, and the total cross section for *p-p* scattering could be determined from a knowledge of the incident proton flux. The range distribution curves from which the results were derived are given. The possibilities for extending the method to particles of higher energy are discussed, along with improvements in photographic technique (emulsions, etc.).

The scattering of 4.2 Mev protons by deuterium, helium, and other light elements, H. Heitler, A. May, C. Powell, *Proc. Roy. Soc.*, **190A,** 180–195 (1947). Photographic methods of detection were used to determine the angular distribution of scattering. The scatterers were deuterium, helium, nitrogen, oxygen, neon, argon, chlorine, and bromine. The results for most of the elements are describable in terms of a Coulomb interaction on the incident *S* wave. Several inelastic scatterings (*e.g.*, neon) were investigated. Some further scattering theory is included, and comparison made with the results of other investigators.

The elastic scattering of 6.5 Mev deuterons, helium, and other light elements, Guggenheimer, Heitler, Powell, *Proc. Roy. Soc.*, **190A,** 196–218 (1947). Angular distribution of scattering by deuterium, helium, carbon, nitrogen, oxygen, and neon by photographic methods. For deuterium, oxygen, and helium, the elastically scattered deuterons can be clearly distinguished, and the *P* and *D* terms are found to contribute appreciably to the amplitude of the scattered wave (in contrast to the effect with 4.2 Mev protons, which have about the same velocity). For the other elements the results are confused by tracks resulting from transmutations.

. . . HAROLD BROWN

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